Rotational Barrier and Conjugation: Theoretical Study of Resonance Stabilization of Various Substituents for the Donors NH_2 and OCH_3 in Substituted 1,3-Butadienes

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Abstract: *The barrier to internal rotation around the central C2–C3 single bond of a series of (1E)-monosubstituted 1,3-butadienes and (1E,3E)-1-Y-4-X-disubstituted butadienes, with Y=NH_2 or OCH_3 and X=NO_2, CHO, COOH, CN, CF_3, Cl or F, were studied at the density functional ω B97X-D/6-31G** level. The effect of substituents on π-conjugation in disubstituted 1,3-butadienes was studied by correlating the calculated internal rotational barriers with the difference in structural, atomic and molecular properties between the transition state TS and the s-trans conformers. The calculated differences in lengths of C–C, C–NH_2 and C–OCH_3 single bonds, N-H-N, and C-O-CH_3 angles, NH_2 out-of-plane angle, natural charges on amino nitrogen and methoxy oxygen, and the maximum electrostatic potential on amino hydrogens, were found to correlate strongly with the rotational barriers. The conjugative interaction was strongly stabilized in the case of strong π-electron acceptors such as NO_2 or CHO and is slightly or negligibly affected with Cl and F groups. The resonance stabilization with the remaining acceptors decreases in the order COOH 〉 CN 〉 CF_3. Acceptors X maintain their relative order of stabilization for the two donors, and NH_2 is more stabilizing. Dominant resonance structures are suggested for highly and negligibly conjugated systems.*

Keywords: *1,3-butadiene; rotational barrier; donors and acceptors; conjugation*

■ INTRODUCTION

The conformational characteristics of 1,3-butadiene and substituted 1,3-butadienes have been studied experimentally [1-3] and theoretically [4-7] with the concentration on internal rotation about the central C2–C3 bond. In these studies it was shown that butadiene has two stable conformers, the *s-trans* at a dihedral angle of 180°, and the *s-gauche* at a dihedral angle of 30–40°, with the former being significantly more stable. A predominant transition state, TS(*g-t*), between these two minima occurs around 100°. In addition, another minimum, *s-cis*, is observed at 0° dihedral angle. It was shown that in the orthogonal structure at 90°, the interaction between the two double bonds is lost in *trans*-1,3-butadiene [4,8].

The rotational barrier was shown to be related to the strength of conjugation in a number of studies. These include some nitrogen- and oxygen-substituted 1,3-butadienes [9], silabutadienes [10], germabutadienes [11], and some substituted benzenes and pyrroles [12-16]. In nitrogen- and oxygen-substituted 1,3-butadienes like acrolein, glyoxal, and diaza-1,3-butadienes [9], it was found that shortening of the central C–C bond ongoing from transition states to *s-trans* conformers is largest for 1,3-butadiene where conjugation is relatively most important and smallest for glyoxal which is an unconjugated system. The calculation of potential energy curves of silabutadienes [10] and germabutadienes [11] containing one to four silicon or germanium atoms showed that a short C–C central bond corresponds to large rotational barriers which were correlated with the strength of π-conjugation in the *s-trans* conformers. Lüthi et al. concluded that the presence of both acceptors and donors in linearly π-conjugated oligomers have a cooperative enhancing effect on rotational barrier [17].

The calculated rotational barrier about C–$COCH_3$ bond in a series of para-substituted acetophenones was found to increase as the para substituent is more electron-donor [12]. The increase in barrier height of the internal rotation of the nitro group and the decrease in C–NO_2 bond length in N-substituted-3-nitropyrrole were attributed to the increase in π-conjugation of the nitro group [13]. π-electron acceptors such as CHO, CN or NO_2 were shown to raise the rotational barrier in phenol whereas π-electron donors like OH or F lower the barrier [14].

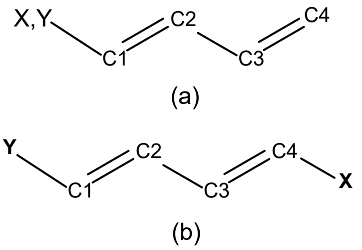
The above studies indicated that rotational barrier increases with conjugation and it reaches its largest value in strong acceptor-strong donor combinations provided steric hindrance and intramolecular hydrogen bonding are avoided. However, they didn't establish any scale for the ability of certain donors to stabilize a given acceptor and vice versa in 1,3-butadiene. Moreover, the extent of conjugation was explained in terms of the change of only one bond length, and even in this case, no linear correlation with rotational barrier was established.

Some methods have been examined for quantitative measurement of resonance in substituted compounds with the aim of arranging the strength of several donors with respect to a given acceptor and vice versa. One method which showed a variable success is that of Taft [18-20] and requires the evaluation of different forms of resonance constants with several corrections to fit the experimental data. A second approach is the evaluation of the resonance interaction energies of substituents through the calculation of isodesmic and homodesmotic reactions [21-23]. However, this method has the problem of selecting the proper similar saturated and unsaturated systems to be compared and also the interference of other factors like polarization on the calculated interaction energy of substituents.

Clearly, there is a need to construct a scale in which one can arrange several donors according to their ability to stabilize a given acceptor and vice versa. In this work, another approach to the concept of conjugation in terms of rotational barrier in mono and disubstituted 1,3-butadienes is studied, with more emphasis on the later. In particular, the ability of a given group to conjugate with 1,3-butadiene and the ability of the acceptors CHO, NO_2, CN, COOH, CF_3, Cl, and F to conjugate with the donors NH_2 and OCH_3 are discussed. Also, the ability of a given acceptor to maintain its order with both these donors in the constructed scale is examined. The strength of conjugation will be examined by calculation of rotational barrier between the transition state TS(*g*-*t*) and the *s-trans* conformer and correlating it to the change in length of central C–C single bond of butadiene, C–NH_2 and C–OCH_3 bonds, the change in the H-N-H and C-O-CH_3 angles of amino and methoxy groups, respectively, the out-of-plane angle of amino group, the natural charge on amino nitrogen and methoxy oxygen, and the electrostatic potential maxima on amino hydrogens. Finally, resonance structures that account for the π-conjugation in disubstituted 1,3-butadienes will be proposed.

METHODS

Schematic structure of the molecules studied here together with the atom numberings are shown in Scheme 1. The (1*E*)-monosubstituted 1,3-butadienes, and (1*E*,3*E*)-1-Y-4-X-disubstituted butadienes are all in the *s-trans* (*ap*) conformation on the central single bond. The *ap* conformation is selected in order to avoid steric hindrance at low dihedral angle *θ*. Quantum chemical calculations were performed at the density functional ω B97X-D/6-31G** level of theory. The ω B97X-D density functional can accurately predict non-bonded interactions, capable of capturing long and short-range interactions, and can accurately describe charge transfer systems [24]. The internal rotational barrier RB around the central C2–C3 single bond is that between the *s-trans* conformer at a dihedral angle *θ* of 180° and the transition



Scheme 1. Schematic structure and atom numberings for (a) (1*E*)-monosubstituted 1,3-butadienes and (b) (1*E*,3*E*)-1-Y-4-X-disubstituted butadienes. Y=NH_2 or OCH_3. X=CHO, NO_2, COOH, CN, CF_3, Cl, F, or H

state (TS) at θ around 100° that separates it from the *s-gauche* conformation. The effect of conjugation was studied by comparing certain geometric, atomic and molecular parameters in the transition state, where the conjugation is at its smallest, with those in the *s-trans* conformation, where the conjugation is at its largest [25], and correlating that to the rotational barrier. The internal rotation potential energy curves (PECs) were obtained by performing geometry optimization calculations at a set of selected dihedral angle θ values ranging from 0 to 180° with 10° increment. Close to transition state, the increment is decreased to 0.1°. With the exception of dihedral angles θ, all the independent structural parameters were optimized. The out-of-plane angle (θ_{OOP}) is the angle between the amino H-N-H plane and the plane formed between the butadiene carbons and a nitrogen atom. Energies at transition state TSs and *s-trans* conformers are always corrected for zero-point energies. The character of stationary structures was confirmed by vibrational frequencies analyses. All calculations were carried out using Spartan '14 (v. 1.1.4) [26].

■ RESULTS AND DISCUSSION

Monosubstituted 1,3-Butadienes

Table 1 lists the dihedral angles θ of the transition states TSs, rotational barriers RBs between the TS and the *s-trans* conformers, the central C2–C3 bond lengths in the TS and the *s-trans* conformers, and the differences between these bond lengths, all in monosubstituted 1,3-butadienes. All RBs are larger than that of 1,3-butadiene (5.72 kcal/mol) except for RBs of butadienes with Cl and F substituents. With all substituents, the length of the central C2–C3 single bond in the *s-trans* conformer is shorter than that in the TS. However, the differences in bond lengths are not correlated with RBs. Also, the difference in the values of RBs between the substituents is very small (less than 1.4 kcal/mol). Therefore, one cannot establish a reliable order of stabilization among different donors and acceptors in monosubstituted 1,3-butadienes studied here. It will be shown below that the presence of both donors and acceptors result in larger rotational barriers that are correlated strongly with the central C2–C3 single bond as well as other geometric parameters.

Table 1. Calculated rotational barrier (RB) in kcal/mol and geometric parameters of transition state TS and the *s-trans* conformer of the (1*E*)-monosubstituted 1,3-butadienes. Dihedral angle (θ) in degrees and bond distance (R) in Å

Substituent			R (C2–C3)		
X or Y	θ(TS)	RB	TS	*s-trans*	ΔR(C2–C3)[a]
NH_2	100.7	6.85	1.485	1.453	0.032
CHO	99.6	6.48	1.480	1.453	0.027
CN	100.4	6.34	1.482	1.455	0.027
COOH	99.7	6.30	1.481	1.455	0.026
OCH_3	101.3	6.15	1.484	1.455	0.029
NO_2	100.9	6.04	1.481	1.454	0.027
CF_3	101.3	5.77	1.483	1.459	0.024
H	101.1	5.72	1.486	1.461	0.025
Cl	102.3	5.66	1.486	1.459	0.027
F	102.9	5.52	1.485	1.457	0.028

[a] Difference in C2–C3 bond length between TS and *s-trans* conformers

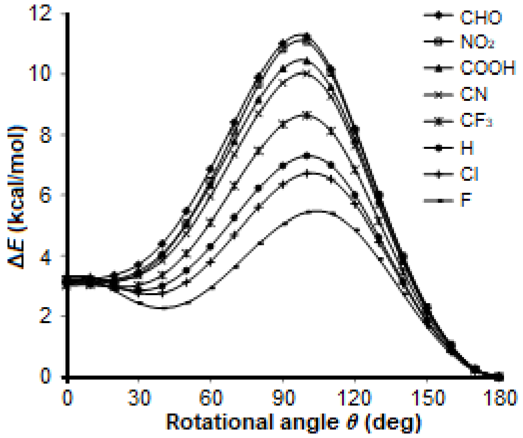


Fig 1. Internal rotation potential energy curves for (1*E*,3*E*)-1-NH_2-4-X- disubstituted butadienes. X denotes the substituents shown in the figure. Energy for each molecule is relative to that of the *s-trans* conformer

Disubstituted 1,3-Butadiene

(1E,3E)-1-NH_2-4-X-disubstituted butadienes

The ω B97X-D/6-31G** internal rotation PECs for (*E*,*E*)-1-NH_2-4-X-disubstituted 1,3-butadienes, where X=NO_2, CHO, COOH, CF_3, H, Cl or F, are shown in Fig. 1. The energy for each molecule is relative to that of *s-trans* conformer of the molecule which is the most stable conformer at a dihedral angle of 180°. The *s-gauche* conformer, which is clearly observed in unsubstituted

1,3-butadiene [1-7], is present only with Cl and F at a dihedral angle around 40°. The *s-cis* conformer at 0° appears with an RB around 3 kcal/mol higher than that of the *s-trans* conformer. The general feature of PEC of 1,3-butadiene [1-7] is preserved only with Cl and F groups. Compared to RB in (*E*)-1-amino-1,3-butadiene (6.85 kcal/mol), the RBs in amino-disubstituted 1,3-butadienes are larger except in the case of Cl (6.28 kcal/mol) and F (5.13 kcal/mol) groups. NO_2 and CHO have the largest values of RB (10.65 and 10.80 kcal/mol, respectively) followed by COOH, CN, CF_3, Cl, and F in that order. The RB value with F substituent (5.13 kcal/mol) is even smaller than that of unsubstituted 1,3-butadiene (5.72 kcal/mol, Table 1).

Table 2 lists the dihedral angles θ for the transition states TSs, the rotational barriers RBs between the TS and *s-trans* conformers, and the differences in some geometric, atomic and molecular parameters between these two conformers, all for (1*E*,3*E*)-1-NH_2-4-X-disubstituted butadienes. The parameters include the central C2–C3 single bond lengths, C1–NH_2 bond lengths, H-N-H bond angles and out-of-plane angles of the NH_2 group [17], natural charges on amino nitrogen [27-28], and maxima of the electrostatic potential on amino hydrogens [28,30]. The chosen parameters are the ones that are expected to be more affected by the extent of conjugation.

The substituents in Table 2 are arranged in order of decreasing RBs. The RB values given in Table 2 are significantly higher than those of corresponding monosubstituted 1,3-butadienes (Table 1). As in the case of monosubstituted 1,3-butadienes, the central C2–C3 bond in the amino-disubstituted 1,3-butadienes is shorter at the *s-trans* position compared to those of the TS; however, the difference is larger in the disubstituted 1,3-butadienes. The same situation is also valid for C1–NH_2 bond.

To test whether the order of substituents with respect to RBs reflects the order of strength of π-conjugation, these RBs are correlated with the shortening of central C2–C3 and terminal C1–NH_2 single bonds, the change of geometry around N atom in NH_2, and the change in natural charges. Here, the changes in these geometric and atomic parameters between *s-trans* and TS states are correlated with the changes in RBs between these states.

Fig. 2 shows that the relationship between RBs and changes in C2–C3 and C1–NH_2 bond lengths are rather linear. These two bond lengths in *the s-trans* state are shorter than those in TS state. Amino-disubstituted 1,3-butadienes with the acceptors CHO and NO_2 have the highest RBs and the largest changes in both bond lengths. These are followed by molecules with the substituents COOH, CN, CF_3, Cl, and F in this order of decreasing RBs and changes in the two bond lengths.

It is expected that as the lone pair on NH_2 becomes so highly involved in the conjugation, the geometry around N atom changes from pyramidal to almost planar [27,31]. This is confirmed by the sum of three angles

Table 2. Calculated rotational barrier (RB) in kcal/mol and geometric parameters of transition state TS and the *s-trans* conformers of the (1*E*,3*E*)-1-NH_2-4-X-disubstituted butadienes. Dihedral angle (θ) in degrees, bond distance (R) in Å, bond angle (A) and out-of-plane angle (θ_{OOP}) in degrees, and maximum electrostatic potential (max. EP) in kJ/mol. Δ denotes the difference of bond distance, angle, or natural charge (Q_n) between TS and *s-trans* conformers

Substituent X	θ(TS)	RB	ΔR(C2–C3)	ΔR(C1–NH_2)	ΔA(H-N-H)	$\Delta\theta_{OOP}$	ΔQ_n	Δmax. EP
F	94.0	5.13	0.029	0.002	0.17	0.89	0.005	6.51
Cl	102.2	6.28	0.033	0.007	0.9	3.47	0.009	15.72
H	100.7	6.85	0.032	0.008	1.11	3.86	0.010	17.98
CF_3	98.5	8.32	0.038	0.017	2.48	9.89	0.017	30.87
CN	99.1	9.56	0.042	0.019	2.85	12.77	0.022	37.59
COOH	97.4	9.96	0.043	0.023	3.36	14.16	0.024	
CHO	96.9	10.80	0.045	0.024	3.55	15.38	0.026	45.71
NO_2	96.8	10.65	0.047	0.025	3.88	20.86	0.029	50.63

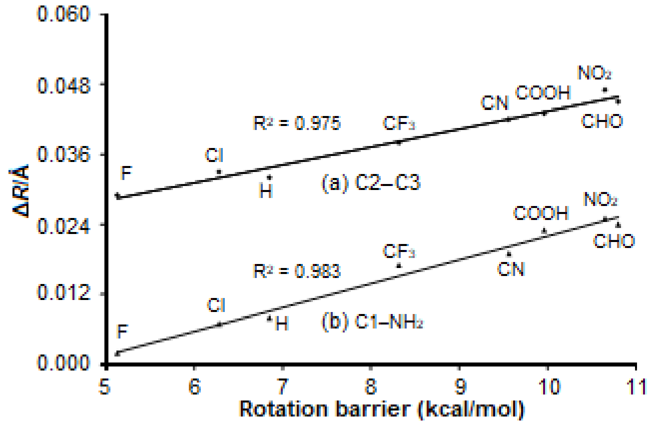


Fig 2. The difference in (a) C2–C3 and (b) C1–NH_2 bond lengths *R* between the transition state TS and *s-trans* conformers versus rotational barrier of (1*E*,3*E*)-1-NH_2-4-X-disubstituted butadienes. X denotes the substituents shown in the figure

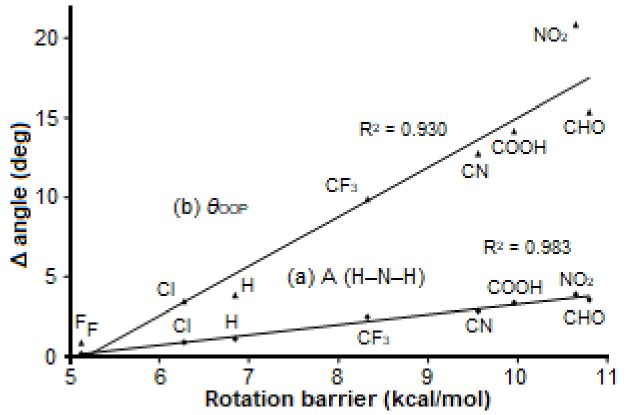


Fig 3. The difference in amino (a) *A*(H-N-H) and (b) out-of-plane θ_{OOP} angles between the transition state TS and *s-trans* conformers versus rotational barrier of (1*E*,3*E*)-1-NH_2-4-X-disubstituted butadienes. X denotes the substituents shown in the figure

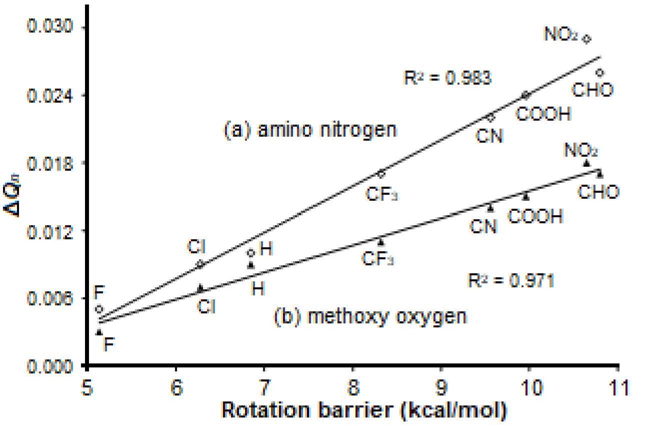


Fig 4. The difference in natural charge Q_n on (a) amino nitrogen of (1*E*,3*E*)-1-NH_2-4-X-disubstituted butadienes and (b) methoxy oxygen of (1*E*,3*E*)-1-OCH_3-4-X-disubstituted butadienes, versus rotational barrier. In both, the difference is between the transition state TS and *s-trans* conformers. X denotes the substituents shown in the figure

around N atom in the *s-trans* conformers. The sum of angles around N atom is almost that of a planar NH_2 with the substituents NO_2 (357°) and CHO (354°), whereas with F and Cl substituents, on the other extreme, it differs by 14–17° from the planar geometry. Also, the change of the amino H-N-H angle and the out-of-plane angle θ_{OOP} between *s-trans* conformer and TS are linearly correlated with the increase in RB as shown in Fig. 3. The order of substituents is the same as that in Fig. 2.

The natural charge on amino nitrogen was shown to correlate very well with C–NH_2 bond lengths in aniline compounds [27-28]. The change in natural charge (ΔQ_n) on amino nitrogen between *s-trans* conformer and TS is shown in Fig. 4(a) to be very linearly correlated with RB, with the same substituents order in the previous figures.

The maximum (positive) electrostatic potential sites [28,30] are around the hydrogen atoms of the amino group in disubstituted 1,3-butadienes studied here except for the TS of COOH substituent where the maximum of electrostatic potential lies on hydrogen or carboxy group. It is expected that as conjugation is enhanced, the value of electrostatic potential maxima is increased and NH_2 groups, therefore, become more hydrogen donor (less basic) since electron density is shifted away from amino hydrogens. Fig. 5 shows that the difference in electrostatic potential maxima between the *s-trans* and the TS conformers is strongly correlated with RB.

(1E,3E)-1-OCH₃-4-X-disubstituted butadienes

The ω B97X-D/6-31G** internal rotation PECs for (1*E*,3*E*)-1-OCH_3-4-X-disubstituted butadienes, where X=NO_2, CHO, COOH, CF_3, H, Cl or F, are shown in Fig. 6.

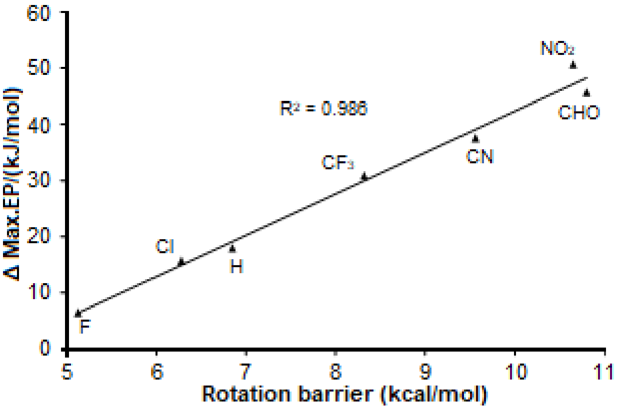


Fig 5. The difference in maximum electrostatic potential between the transition state TS and *s-trans* conformers versus rotational barrier of (1*E*,3*E*)-1-NH_2-4-X-

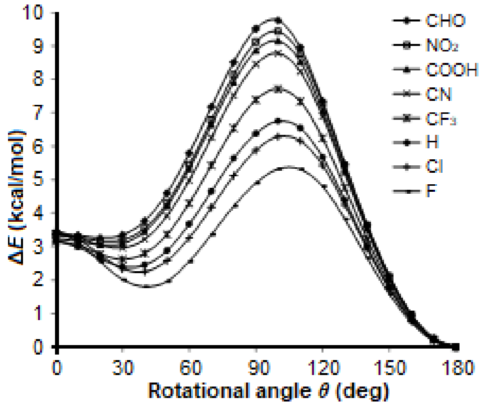


Fig 6. Internal rotation potential energy curves for (1*E*,3*E*)-1-OCH_3-4-X-disubstituted butadienes. X denotes the substituents shown in the figure. Energy for each molecule is relative to that of the *s-trans* conformer

Table 3. Calculated rotational barrier (RB) in kcal/mol and geometric parameters of transition state TS and the *s-trans* conformers of the (1*E*,3*E*)-1-OCH_3-4-X- disubstituted butadienes. Dihedral angle (θ) in degrees, bond distance (R) in Å, bond angle (A) in degrees. Δ denotes the difference of bond distance, angle, or natural charge (Q_n) between TS and *s-trans* conformers

Substituent X	θ (TS)	RB	Δ*R*(C2–C3)	Δ*R*(C1–OCH3)	Δ*A*(C1-O-CH3)	ΔQ_n
F	105.2	4.97	0.029	0.001	0.05	0.003
Cl	103.8	5.78	0.031	0.003	0.23	0.007
H	101.3	6.15	0.029	0.005	0.33	0.009
CF_3	100.9	7.12	0.033	0.008	0.42	0.011
CN	98.8	7.91	0.038	0.010	0.49	0.014
COOH	98.7	8.21	0.037	0.011	0.49	0.015
CHO	97.8	8.82	0.039	0.013	0.57	0.017
NO_2	98.9	8.44	0.040	0.013	0.60	0.018

As in the case of amino-disubstituted 1,3-butadienes, the general feature of PEC of unsubstituted 1,3-butadiene is preserved only in the presence of Cl and F groups. Table 3 disubstituted butadienes. X denotes the substituents shown in the figure lists the dihedral angles θ for the transition states TSs, the rotational barriers RBs between the TSs and *s-trans* conformers together with some geometric and atomic parameters in going from TSs to *s-trans* conformers, all for (1*E*,3*E*)-1-OCH_3-4-X-disubstituted butadienes. The geometric and atomic parameters include the central C2–C3 and C–OCH_3 bond lengths, the C1-O-CH_3 bond angles, and the formal charges on methoxy oxygen. The order of substituents in terms of RBs is the same as that observed in amino-disubstituted 1,3-butadienes, but the values of RBs are smaller.

RB exhibits a very linear relationship with Δ*R*(C2–C3) and Δ*R*(C1–OCH_3), Δ*A*(C1-O-CH_3), and changes in natural charges (ΔQ_n), as shown in Fig. 7, 8, and 4(b), respectively. The order of substituents in the relation between RBs and the changes in bond lengths, angles, and natural charges is the same as that in 1(*E*,*3E*)-1-NH_2-4-X-butadienes but the changes in these parameters are relatively smaller in (1*E*,3*E*)-1-OCH_3-4-X-butadienes especially Δ*A*(C1-O-CH_3). The RB in (1*E*,3*E*)-1-OCH_3-4-Cl-butadiene (5.78 kcal/mol) is slightly smaller than that in (1*E*)-OCH3-1,3-butadiene (6.15 kcal/mol) but it is noticeably smaller in (1*E*,3*E*)-1-

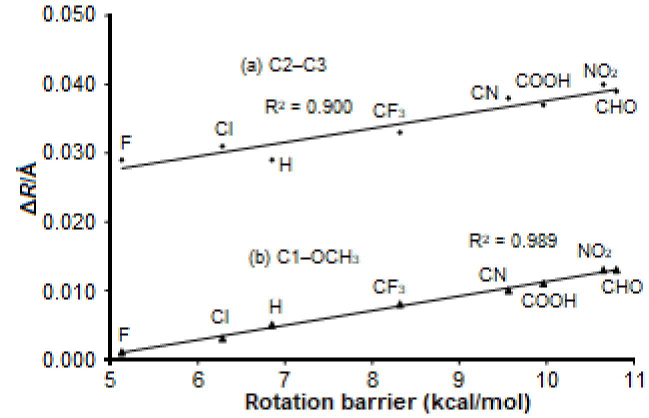


Fig 7. The difference in (a) C2–C3 and (b) C1–OCH_3 bond lengths *R* between the transition state TS and *s-trans* conformers versus rotational barrier of (1*E*,3*E*)-1-OCH_3-4-X-disubstituted butadienes. X denotes the substituents shown in the figure

OCH$_3$-4-F-butadiene (4.97 kcal/mol) compared to (1*E*)-OCH_3-1,3-butadiene.

The Order of Resonance Stabilization of Common Acceptors for the Donors NH_2 and OCH_3

Fig. 2–4, 6 and 7 clearly show that the value of rotational barrier is a measure for the extent of π-conjugation especially when the barrier height is proportional to geometric, atomic and molecular parameters that reflect the degree of conjugation. The fact that the order of substituents with respect to both donors NH_2 and OCH_3 in the above figures is the same indicates that a scale can be constructed based on the ability of a given acceptor to stabilize these two donors. This ability decreases in the order CHO, NO_2 ⟩ COOH ⟩ CN ⟩ CF_3 ⟩ Cl ⟩ F. RBs and Δ*R*(C2–C3) in disubstituted butadienes with F and, to a less extent; Cl substituents, are smaller than those in monosubstituted amino and methoxy butadienes. Also, as mentioned above, the RB in (1*E*,3*E*)-1-NH_2-4-F-butadiene is even smaller than that in unsubstituted 1,3-butadienes. Therefore, it can be concluded that Cl and F are not involved in π-conjugation in disubstituted 1,3-butadiene and that F is slightly destabilizing. This implies that the σ–the electron-withdrawing inductive effect of F atom is negligible in the π-electrons resonance system here and in fact a small mesomeric electron-releasing effect is to be suggested [32-33]. Because of the RBs and the changes in the geometric parameters in (1*E*,3*E*)-1-NH_2-4-X-butadienes are higher than the corresponding ones in (1*E*,3*E*)-1-OCH_3-4-X-butadienes, it can be suggested that NH_2 is a better donor than OCH_3. Also, since RBs and Δ*R*(C2–C3) in disubstituted 1,3-butadienes are significantly larger than monosubstituted 1,3-butadienes, it can be inferred that an appreciable increase in resonance stabilization is due to the cooperative effect of both donors and acceptors even if they are not very strong. In the presence of only a strong donor like NH_2 or a strong acceptor-like CHO, the RB increases by 0.76–1.1 kcal/mol compared to that in unsubstituted 1,3-butadiene (Table 1). On the other hand, the RB in disubstituted 1,3-butadienes is between 2.6-5.1 kcal/mol higher than that of unsubstituted 1,3-butadiene excluding the Cl and F groups (Tables 2, 3). The resonance stabilization in the presence of both acceptor and donor in the 1*E*,3*E*-1,4 positions in 1,3-butadienes is due to extending the conjugation throughout the whole molecule. The shortening of the C1–NH_2 and C1–OCH_3 bonds with the increase in RB are evidence for the involvement of these bonds in conjugation. Extending the conjugation in disubstituted 1,3-butadiene will be elaborated in the discussion of the preferable resonance structures below.

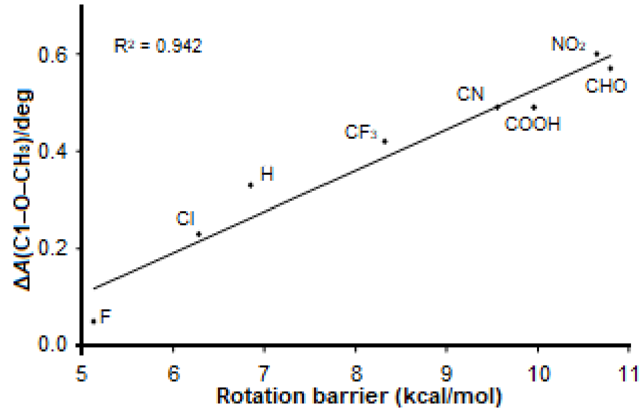


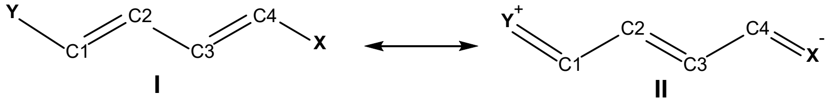
Fig 8. The difference in C1–O–CH_3 angle *A* between the transition state TS and *s-trans* conformers versus rotational barrier of (1*E*,3*E*)-1-OCH_3-4-X-disubstituted butadienes. X denotes the substituents shown in the figure

Resonance structures

Two important resonance structures can be drawn for disubstituted 1,3-butadienes [12c] as shown in Scheme 2.

In order to find the dominant resonance structure for the cases of highly conjugated systems and systems with weak or negligible π-conjugation, a comparison is made between the length of the three CC bonds of the butadiene, C1–NH_2 and C1–OCH_3 bond lengths, and the natural charges on amino nitrogen, methoxy oxygen, and C4 of butadiene, all for the *s-trans* conformers of disubstituted 1,3-butadienes. Tables 4, 5 list the values of these parameters together with carbon-acceptor (C1–X) bond length in monosubstituted 1,3-butadienes (refer to Scheme 1 for atom numbering). It can be seen from the tables that as conjugation is enhanced, the C1=C2 and C3=C4 bond lengths are increased in both the amino and methoxy derivatives and it is almost similar to those of amino and methoxy monosubstituted 1,3-butadienes (acceptor H in Table 4, 5) in the cases of Cl and F substituents.

On the other hand, as shown above, the C2–C3, C1–NH_2, and C1–OCH_3 bonds have a more double bond character as conjugation is enhanced. It can be also observed from data in Table 4, 5 that the C4–X bond



Scheme 2. Two important resonance structures for disubstituted 1,3-butadienes. Y=NH_2 or OCH_3 and X=CHO, NO_2, COOH, CN, CF_3, Cl, F, or H

Table 4. Single and double bond lengths and natural charges Q_n (on amino nitrogen and C4 of butadiene) for the *s-trans* conformers of (1*E*,3*E*)-1-NH_2-4-X-disubstituted butadienes. For atom, numbering see Scheme 1

Substituent	Bond distance (Å)							Q_n	Q_n
X	C1=C2	C3=C4	C2–C3	C1–NH_2	C4–X	C1–X[a]	(C1–X)–(C4–X)	(N)	(C4)
F	1.343	1.330	1.453	1.386	1.346	1.338	-0.008	-0.870	0.215
Cl	1.345	1.334	1.450	1.379	1.744	1.737	-0.007	-0.864	-0.277
H	1.344	1.337	1.453	1.384	1.084	1.084	0.000	-0.869	-0.477
CF_3	1.348	1.338	1.444	1.370	1.486	1.492	0.006	-0.857	-0.398
CN	1.352	1.349	1.438	1.364	1.425	1.428	0.003	-0.849	-0.405
COOH	1.351	1.346	1.437	1.365	1.464	1.475	0.011	-0.851	-0.411
CHO	1.353	1.351	1.434	1.363	1.462	1.475	0.013	-0.848	-0.409
NO_2	1.355	1.343	1.432	1.357	1.437	1.451	0.014	-0.841	-0.177

[a]bond length for *s-trans* conformers of (1*E*)-monosubstituted 1,3-butadienes

Table 5. Single and double bond lengths and natural charges Q_n (on methoxy oxygen and C4 of butadiene) for the *s-trans* conformers of the (1*E*,3*E*)-1-OCH_3-4-X-disubstituted butadienes. For atom, numbering see Scheme 1

Substituent	Bond distance (Å)							Q_n	Q_n
X	C1=C2	C3=C4	C2–C3	C1–OCH_3	C4–X	C1–X[a]	(C1–X)–(C4–X)	(O)	(C4)
F	1.337	1.330	1.453	1.353	1.343	1.338	-0.005	-0.534	0.229
Cl	1.338	1.333	1.452	1.349	1.742	1.737	-0.005	-0.528	-0.263
H	1.337	1.336	1.455	1.352	1.084	1.084	0.000	-0.531	-0.460
CF_3	1.340	1.336	1.448	1.344	1.489	1.492	0.003	-0.524	-0.379
CN	1.342	1.347	1.442	1.340	1.426	1.428	0.002	-0.519	-0.384
COOH	1.342	1.344	1.442	1.342	1.468	1.475	0.007	-0.521	-0.390
CHO	1.343	1.347	1.440	1.340	1.467	1.475	0.008	-0.519	-0.390
NO_2	1.344	1.339	1.438	1.336	1.443	1.451	0.008	-0.514	-0.157

[a]bond length for *s-trans* conformers of (1*E*)-monosubstituted 1,3-butadienes

lengths in disubstituted systems are shorter than the corresponding ones in the monosubstituted systems (C1–X bonds) and the difference between the two increases with conjugation. From the comparison between mono and disubstituted butadienes**,** it is clear that the simultaneous presence of donors and acceptors is the main cause of resonance stabilization. Finally, Tables 4 and 5 show that the natural charges on amino nitrogen and methoxy oxygen atoms of disubstituted 1,3-butadienes become less negative as conjugation is enhanced which is due to the involvement of electron density around nitrogen and oxygen atoms in conjugation. This, together with shortening of the $C1–NH_2$, $C–OCH_3$, and central C2–C3 bonds, the change of geometry around amino nitrogen and methoxy oxygen atoms from pyramidal to planar, and the increase in electrostatic potential maxima around amino hydrogens are more evidence that π-conjugation extends to include $C1–NH_2$ and $C1–OCH_3$ bonds. Based on the above discussion, it can be concluded that structure II in Scheme 2 is dominant for the highly π-conjugated systems.

For the weak or negligible resonance systems (mainly with Cl and F groups), the structure I is the most important since C1=C2, C2–C3, $C1–NH_2$, and $C1–OCH_3$ bonds lengths in disubstituted butadienes are almost those of amino and methoxy monosubstituted butadienes. This confirms the negligible effects of F and Cl groups on conjugation in disubstituted 1,3-butadienes even in the presence of strong donors in the *ap*-conformation studied here. The last column in Table 4, 5 shows that the formal charge on C4 is positive in the case of F and is less negative with Cl and NO_2 compared to other substituents. This is due to inductive electronegativity effects of F, Cl and nitro oxygen which is directed on the sigma skeleton of butadiene and not the π-conjugation system. Actually, as mentioned above, F acted here as a destabilizing electron donor.

As noted in this study, the RBs were correlated with changes in geometric, atomic and molecular properties between the *s-trans* and TS conformers and not versus these parameters in the *s-trans* states. This approach adopted here, besides giving better correlations, is more sensible because the rotational barriers are measured between these two limits. A similar approach with substituted anilines and anisoles (not yet published) gave similar order of resonance stabilization of substituents for amino and methoxy groups. This gives further confidence of the validity of considering the changes in geometric, atomic and molecular parameters between the *s-trans* and TSs states. The qualitative correlations of geometric and atomic parameters of *s-trans* conformers with RBs were made mainly to draw the most likely resonance forms for the most and least resonance stabilizing substituents.

CONCLUSION

The ω B97X-D/6-31G** calculations show that the rotational barrier RB between the TS and *s-trans* conformations of (1*E*,3*E*)-1-Y-4-X-disubstituted butadienes, with the donors Y being NH_2 or OCH_3 and different substituents X, is a reliable method for measuring the relative strength of π-conjugation in disubstituted 1,3-butadienes. The extent of conjugation is verified by the shortening of the central C2–C3 and the terminal $C1–NH_2$ and $C1–OCH_3$ single bonds, the increase in planarity around amino nitrogen and methoxy oxygen, the decrease in negativity of natural charges on amino nitrogen and methoxy oxygen, as well as the increase in electrostatic potential maxima, when RB is increased. The scale of stabilization of different substituents for the donors NH_2 and OCH_3 decreases in the order $NO_2 \sim CHO \rangle COOH \rangle CN \rangle CF_3 \rangle H \rangle Cl \rangle F$, and NH_2 is found to be more stabilizing than OCH_3. Significant resonance stabilization is due to the simultaneous presence of both acceptor and donor at either end of 1,3-butadiene. A resonance structure for highly conjugated systems is suggested where the conjugation extend over the whole molecules whereas in disubstituted 1,3-butadienes with Cl and F groups it is similar to that of monosubstituted amino or methoxy 1,3-butadienes.

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