DOI: 10.1002/chem.200501517

Stereoelectronic Effects on Type I 1,2-Dyotropic Rearrangements in Vicinal Dibromides

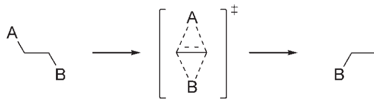
Israel Fernández,*[a, b] Miguel A. Sierra,[a] and Fernando P. Cossío[c]

Abstract: The effects of different substituents on type I-dyotropic rearrangements of open-chain and cyclic 1,2-dibromo hydrocarbons have been studied by means of DFT calculations. The activation energy (E_a) of this transformation decreases with the π-donor ability of the substituent attached to the reacting ethylenic system. This is due to donation of electronic density by conjugation or hyperconjugation. This donation leads to longer C–C and C–Br bond lengths in the corresponding four-membered transition states (TSs). Linear relationships between the E_a and either the σ_p Hammett substituent constants and the C–C bond length of the TSs were also found. In all cases, the processes have a high value of synchronicity, which is mainly independent on the substituents. A model based on the second-order perturbational analysis for one ethylene unit with two apical bromine radicals accounts for all the computed results.

Keywords: density functional calculations • dyotropic rearrangements • stereoelectronic effects • synchronicity

Introduction

The type I 1,2-dyotropic rearrangement is defined as the simultaneous intramolecular migration of two σ bonds which interchange their relative positions in a stationary scaffold (Scheme 1).[1] This process occurs concertedly through the bicyclic transition state as depicted in Scheme 1. Recently, we proposed[2] a stepwise mechanism for a dyotropic rearrangement in the photoreaction of chromium(0) aminophosphino (Fischer) carbenes. Our report was simultaneous to the proposal by Houk[3] of a non-concerted dyotropic rearrangement of *N*-(α-silyl)allyl amides to *cis*-enamides.



Scheme 1.

In the particular case of dyotropic reactions in vicinal dibromides, there are several important papers on the nature of the experimentally observed mutarotations in 1,2-dibromocyclohexanes[4] and 5,6-dibromocholestanes[5,6] (Scheme 2). Thus, in a seminal work Grob and Winstein[5] discussed the possible mechanisms of these reactions and concluded that "…mutarotation does not involve dissociation of the steroid dibromide to bromonium ion and bromide ion, followed by return of external bromide ion. The important mode of isomerization is therefore a so-called internal one. (…) It is considered probable that (…) an intermediate or transition state is involved with negligible charge separation, both bromine atoms being essentially equivalent". The features of these hypothetical structures would be those shown in Scheme 1. In a subsequent paper, Barton and Head[6] suggested that these structures are transition states and not reaction intermediates. More recent computational[7] and experimental works[8] carried out on type I 1,2-

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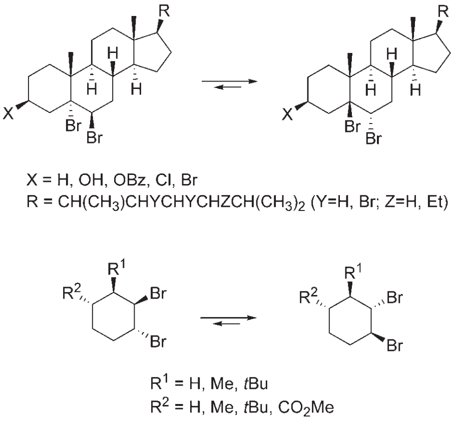
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: Cartesian coordinates (in Å) and total energies (in a.u., non corrected zero-point vibrational energies included) of all transition states discussed in the text.



Scheme 2. Experimentally studied dyotropic reactions in cyclic vicinal dibromoalkanes.

dyotropic rearrangements have shown that the activation energy of dyotropic processes depends, mainly, on the delocalization of the π system being developed in the corresponding transition states (Scheme 1). These aspects of the reaction offer a good opportunity to develop a model to account for the influence of stereoelectronic effects[9] both in the synchronicity and energy barriers of dyotropic processes. Reported herein is the systematic DFT study of these effects, correlating Hammett's σ_p parameters and some geometrical features of the dyotropic TS with the E_a of these processes.

Computational Details

All the calculations reported in this paper were obtained with the Gaussian 03 suite of programs.[10] Electron correlation has been partially taken into account using the hybrid functional usually denoted as B3LYP[11] and the standard 6-31+G* and 6-31G* basis sets[12] for hydrogen, carbon, oxygen, nitrogen, and sulphur, and the Hay–Wadt small-core effective core potential (ECP) including a double-ξ valence basis set[13] for bromine or chlorine (LanL2DZ keyword). Zero-point vibrational energy (ZPVE) corrections have been computed at the B3LYP/6-31+G* level and have not been corrected. Stationary points were characterized by frequency calculations,[14] and have positive definite Hessian matrices. Transition structures (TSs) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[15]

Abstract in Spanish: *Mediante cálculos DFT se han estudiado los efectos de distintos sustituyentes en reordenamientos diotrópicos de tipo I en 1,2-dibroalcanos tanto de cadena abierta como cíclicos. La energía de activación (*E_a*) de este proceso disminuye con el carácter π-dador del sustituyente unido al sistema etilénico reactivo. Este efecto se debe a la donación de densidad electrónica por parte del sustituyente mediante conjugación o hiperconjugación. Esta donación provoca que las distancias de enlace C–C y C–Br sean más largas en los correspondientes estados de transición (ET) de cuatro miembros. Se han encontrado correlaciones lineales tanto entre* E_a *y las constantes* σ_p *de Hammett con la distancia C–C en los distintos ET's. En todos los casos, los procesos poseen altos valores de sincronicidad, la cual es prácticamente independiente del sustituyente. Se ha propuesto un modelo basado en la teoría de perturbaciones de segundo orden para explicar los resultados obtenidos.*

We computed the synchronicity (S_y) of the dyotropic rearrangements shown in Schemes 3, 5 and 6 using the following Equation:[16]

$$S_y = 1 - \frac{\sum_{i=1}^{n} \frac{|\delta B_i - \delta B_{\mathrm{AV}}|}{\delta B_{\mathrm{AV}}}}{2n-2} \qquad (1)$$

where n is the number of bonds directly involved in the reaction and δB_i stands for the relative variation of a given bond index B_i at the transition state (TS), according to the following formula:

$$\delta B_i = \frac{B_i^{\mathrm{TS}} - B_i^{\mathrm{R}}}{B_i^{\mathrm{P}} - B_i^{\mathrm{R}}} \qquad (2)$$

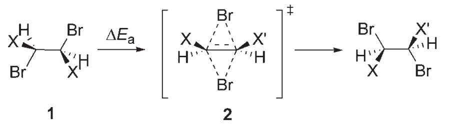
where the superscripts R and P refer to the reactants and the product, respectively. The average value of δB_i, denoted as δB_{AV} is therefore:

$$\delta B_{\mathrm{AV}} = n^{-1} \sum_{i=1}^{n} \delta B_i \qquad (3)$$

The Wiberg bond indices[17] B_i have been computed by using the natural bond orbital (NBO) method.[18]

Results and Discussion

The dyotropic reaction of 1,2-dibromoethane (**1a**) (Scheme 3) was considered first. This process occurs through the four-membered transition state **2a** in a concerted pathway.

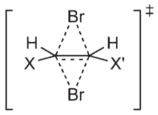


Scheme 3.

The D_{2h} symmetry of **2a** and the high calculated value of synchronicity ($S_y = 0.87$) indicate that this transformation is perfectly synchronous, as expected based on the reported results.[7] The C–C distance in the transition state **2a** has a partial double-bond character (r = 1.416 Å, NBO bond order = 1.3). The deviation of 0.13 units from perfect synchronicity (S_y = 1.00) is attributable to the partial double bond character of the stationary system. This partial delocalization is not explicitly included in the evaluation of the synchronicity since the static C–C bond does not change its bond order on going from the reactant to the product. However, the partial double bond character of the C–C moiety at **2a** promotes a C−Br bond order lower than 0.5 thus resulting in a S_y value lower than 1.0. Therefore, the definition of synchronicity reported in Equation (1) reflects bonding changes present in the TS and not in the reactants or products.

As stated above, delocalization of the newly formed π bond in the transition state is proposed to lower the E_a of the dyotropic rearrangement. The transition state of 2,3-dibromobutane **2b**-*cis* and **2b**-*trans* (Table 1, entries 2 and 3) have a lower activation energy ($\Delta E_a = 4.7$ and 5.0 kcal mol^{-1}, respectively) and longer C–C ($\Delta r = 0.016$ and 0.012 Å) and C–Br ($\Delta r = 0.072$ and 0.075 Å) distances compared with **2a**. This is a good evaluation of the hyperconjugative effect exerted by each Me group in the transition state. This effect should not be involved in stabilization of the π bond, but in the interaction with the σ* C−Br. On the other hand, the hyperconjugative effect of the Me-groups on the synchronicity of the process respect to **2a** is small albeit measurable ($\Delta S_y = 0.11$ in both cases).

Table 1. Selected bond lengths, activation energies and synchronicities for the dyotropic reactions of the Scheme 3.



2a-m

Entry	TS	r(C–C) [Å]	E_a [kcal mol^{-1}]	S_y
1	**2a**, X=X'=H	1.416	28.2	0.87
2	**2b**-*cis*, X=X'=Me	1.432	23.5	0.76
3	**2b**-*trans*, X=X'=Me	1.428	23.2	0.76
4	**2c**, X=H; X'=OH	1.421	22.0	0.75
5	**2d**-*cis*, X=Me; X'=OH	1.429	19.7	0.74
6	**2d**-*trans*, X=Me; X'=OH	1.428	21.2	0.74
7	**2e**-*cis*, X=X'=OH	1.433	16.1	0.72
8	**2e**-*trans*, X=X'=OH	1.432	20.8	0.72
9	**2f**, X=H; X'=NH_2	1.435	14.1	0.72
10	**2g**-*cis*, X=X'=NH_2	1.445	5.8	0.71
11	**2g**-*trans*, X=X'=NH_2	1.451	9.1	0.68
12	**2h**, X=H; X'=Me	1.422	25.5	0.78
13	**2i**, X=H; X'=Cl	1.418	29.3	0.88
14	**2j**, X=H; X'=CN	1.423	29.8	0.79
15	**2k**, X=H; X'=CHO	1.419	28.0	0.80
16	**2l**, X=H; X'=C≡CH	1.428	25.1	0.77
17	**2m**, X=H; X'=NO_2	1.409	33.6	0.80

The effect of electron-donating (EDG) and electron-withdrawing (EWG) groups attached to one or both carbon atoms was calculated next (Scheme 3). Table 1 compiles the calculated E_a and S_y of these 1,2-dibromoethane systems.

The electronic structure of **2a** can be rationalized in terms of the second-order perturbational analysis for one ethylene unit with two apical bromine radicals (Figure 1a). The resulting D_{2h} symmetrical structure exhibits, among other interactions, the combination of one set of $3p_x$ AO's of bromine with the π* orbital of the ethylene unit thus leading to the occupied bonding $1b_{2g}$ combination (HOMO−4) and the unoccupied $2b_{2g}$ antibonding combination (LUMO+1). The other possible two-electron interaction between one symmetry-adapted combination of $3p_z$ AO's of bromine and the π orbital of the ethylene subunit leads to one bonding $2b_{3u}$ combination (HOMO−5) and to the corresponding antibonding $3b_{3u}$ combination, which is the LUMO of the structure. The HOMO is formed by the $4a_g$ unperturbed combination of two $3p_z$ AO's of the bromine pair (Figure 1a). The computed canonical FMO's of **2a** confirm the utility and predicting ability of this perturbational analysis (Figure 1b).

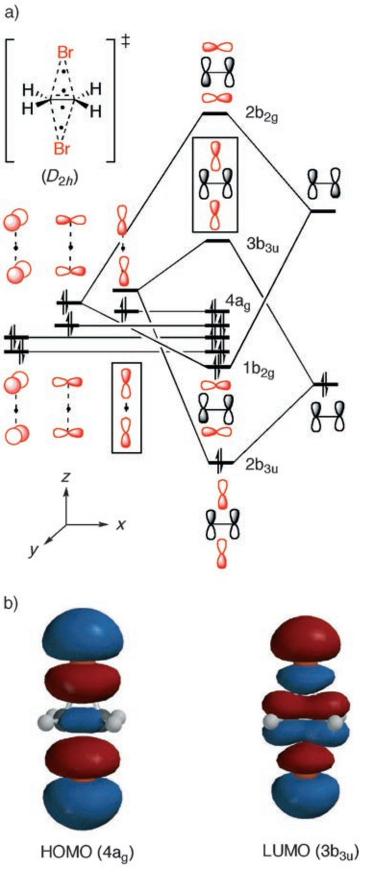
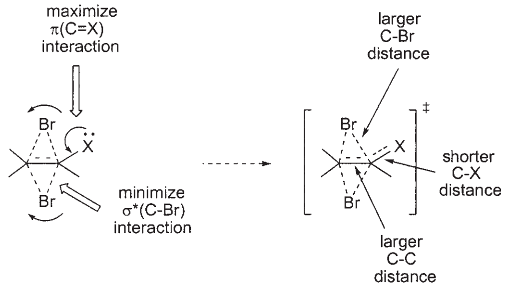


Figure 1. a) Qualitative second-order perturbation diagram associated with the interaction of two bromine radicals and one ethylene subunit (in black), to yield the D_{2h}-symmetric transition structure **2a**. b) Frontier orbitals of **2a**, showing their correspondence with the boxed MO's in Figure 1a.

With this model at hand, the stereoelectronic effects of the substituents can be understood taking into account the interactions between the corresponding atom(s) or group(s) and the topology of the parent LUMO. As we have previously concluded, this orbital can be represented as the combination of an in-phase C=C moiety and an antibonding C−Br contribution (Figure 1b). Therefore, the presence of a π-donating substituent induces a stabilizing two-electron interaction between a filled orbital of the substituent and the parent LUMO, thus producing the elongation of the C−Br bonds contiguous to the donating group in the corresponding TSs (Scheme 4). The same argument leads to an elonga-



Scheme 4. Geometric effects of a π-donating group on the geometry of the TS associated with the corresponding 1,2-dyotropic reaction.

tion of the C–C bond length of the static scaffold and to a contraction of the C–X bond length. For instance, when X = NH_2 the C–C bond lengths are 1.435 and 1.451 Å in **2f** and **2g**-*trans*, respectively, a value significantly larger than that calculated for **2a** (Figure 2). Similarly, the C–Br bond lengths corresponding to the atom attached to the amino group in **2f** are 2.766 Å, whereas in **2a** are of only 2.510 Å. The donation by the amino group is also evidenced in the shortening of the C–NH_2 distance in transition state **2f**. In fact, the latter bond has a partial double-bond character (r = 1.316 Å and NBO bond order = 1.45) in good agreement with the aforementioned geometric effects (Scheme 4).

This analysis based on the stabilizing two-electron interaction between the parent LUMO and one high-energy occupied orbital of the substituent leads to a relative stabilization of the corresponding TS, directly related to the donating ability of the substituent. Therefore, a correlation between one geometric parameter associated with the π character of a given TS and the corresponding activation energy

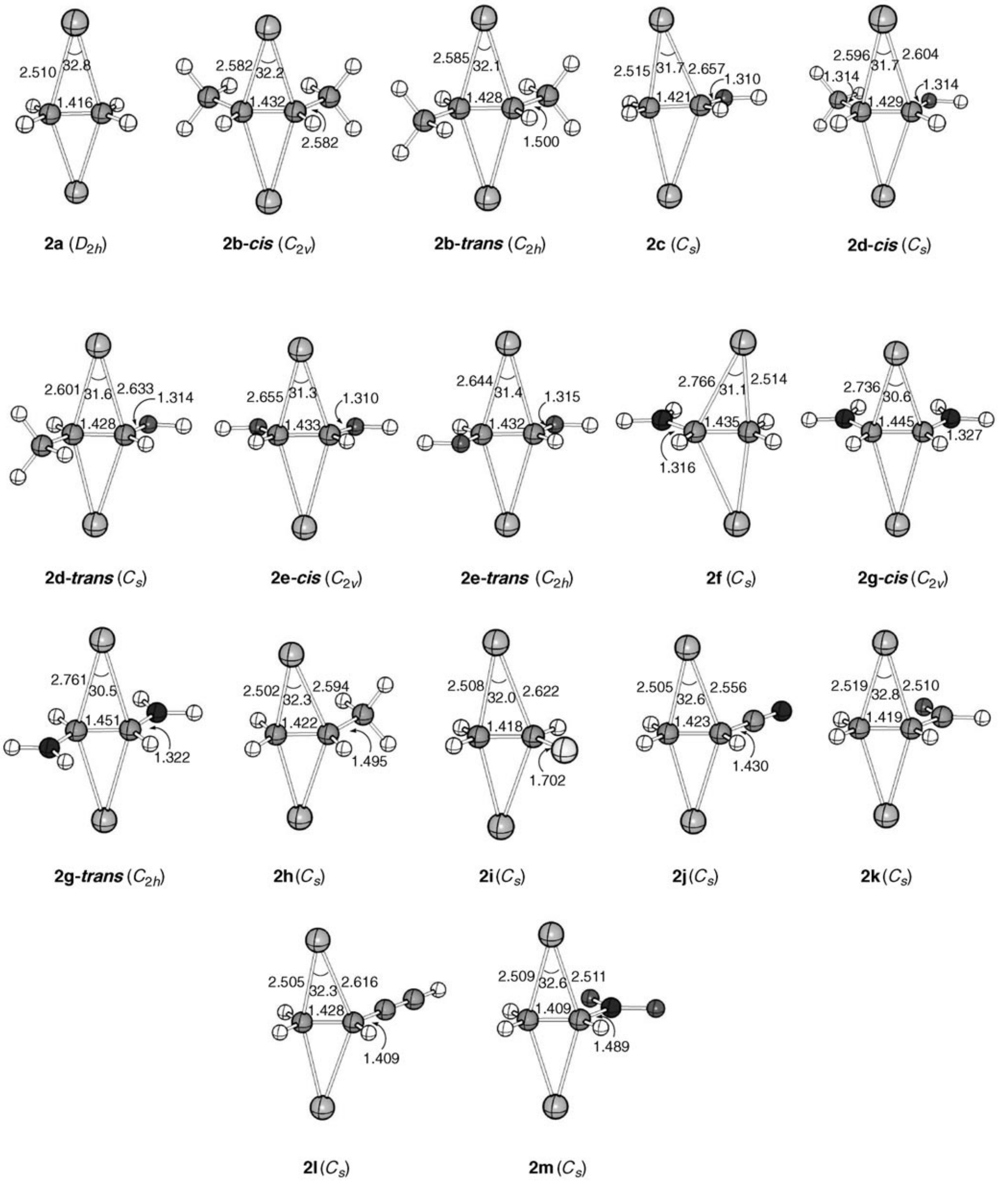


Figure 2. Ball and stick representations of transitions states **2a–m**. All structures correspond to fully optimized B3LYP/LANL2DZ and 6-31+G(d) geometries. Bond lengths and angles are given in Å and degrees, respectively.

must be found. The C–C bond length of the "static" carbon atoms appears to be an appropriate parameter since i) is sensitive enough to the substitution pattern and ii) includes the combined effects of different substituents at different static carbon atoms. The C–Br bond length does not fulfil the second criterion, although reflects very properly the competitive effects of different substituents. For example, in **2c** the superior π-donating ability of the hydroxy group with respect to that corresponding to a methyl group in **2h** results in larger C–Br bond lengths (2.657 Å in **2c** compared with 2.594 Å in **2h**) for the carbon atom contiguous to the hydroxy group (Figure 2). As it can be seen, a good linear relationship with a correlation coefficient of 0.93 and standard error of 2.88 is also found between the activation energies and the C–C bond lengths of the corresponding transition structures (Figure 3). As a general criterion, we can conclude that the larger the C–C bond length of the static scaffold at the corresponding TS, the lower the activation energy. This plot also confirms that the C–C bond is the most appropriate geometric parameter since it is sensitive to the stereochemistry of the substitution in the different transition states. In general, the larger departures from linearity are found for the *cis*-substituted systems probably due to the steric interaction between the donating contiguous groups.

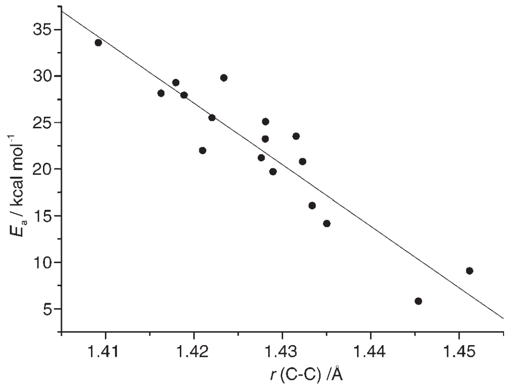


Figure 3. Plot of the activation energies (E_a) versus the C–C bond lengths of the transition states **2a–m**.

As readily seen from the data in Table 1, electron-donating groups facilitate the dyotropic reaction while electron-withdrawing groups lead to higher values of the activation energy of the process. Therefore, it is not surprising that a good correlation between the E_a and the σ_p Hammett substituent constants was found since the latter parameters reflect the extent to which substituents interact with a reaction site through conjugative effect mainly.[19] Thus the plot of E_a versus σ_p for monosubstituted 1,2-dibromoethanes shows a good linear relationship between both parameters with a correlation coefficient of 0.90 and standard error of 2.58 (Figure 4). This clear correlation supports the above statement that the π-donating ability of the substituent induces a stabilization of the corresponding TS and therefore facilitates the dyotropic rearrangement.

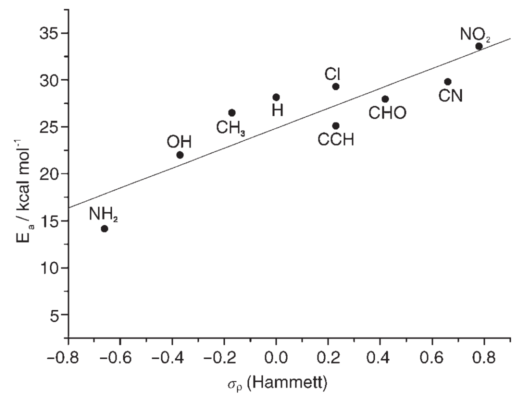
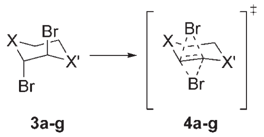


Figure 4. Plot of the activation energies (E_a) versus the σ_p Hammett substituent constants of monosubstituted 1,2-dibromoethanes.

To discuss these processes in more detail, the influence of the geometry in the stabilization of the transition states of dyotropic rearrangement by electron-donating groups was addressed next. The model reaction was the dyotropic reaction of *trans*-1,2-dibromocyclohexane (**3a**; Scheme 5, X = X′ = CH$_2$). An analogous transformation has been experimentally reported[3] in the thermal mutarotation of *trans*-2,3-dibromo-*tert*-butylcyclohexanes.

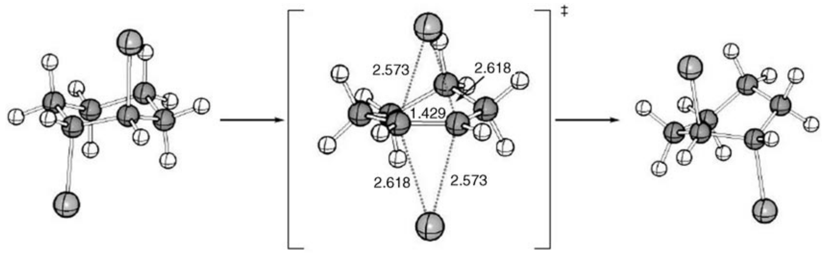


Scheme 5.

This reaction also occurs through a four-membered transition state. Interestingly, the IRC calculations relates this transition state with the twisted-chair **5a** instead of the reported chair[3] (Figure 5). The calculated E_a of this process is 23.6 kcal mol^{-1}, practically identical to the barrier observed for the dyotropic reaction of *cis*-2,3-dibromobutane (entry 2, Table 1). This should be due to the hyperconjugative donating ability of the CH$_2$ groups attached to the reacting carbon atoms that is comparable to the two Me groups of the 2,3-dibromobutane. The effect of donating groups having lone electron pairs was studied next. The results are compiled in Table 2.

Again, we found a clear correlation between the E_a of the dyotropic rearrangement and the donor ability of the heteroatom included in the ring. These results support the trend observed in the open-chain compounds: better π-donor heteroatoms lead to lower activation barriers for dyotropic rearrangements. The stereoelectronic effect of sulphur in the p to σ* transfer is smaller than the observed for the oxygen,[9] therefore its effectiveness to decrease the barrier of the dyotropic rearrangement is the smallest of all the heteroatom six-membered rings computed (Figure 6).

A clear linear relationship with a correlation coefficient of 0.999 and standard error of 0.32 between the E_a for the dyotropic rearrangement and the C–C bond length was



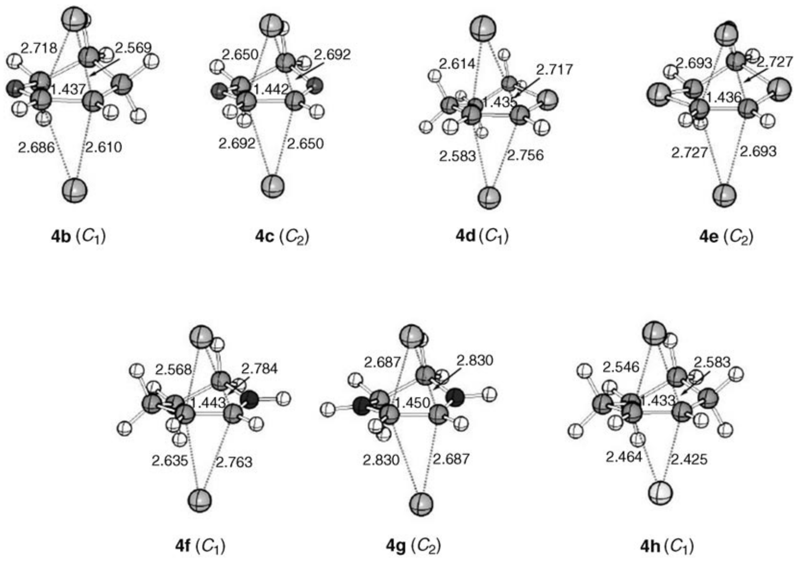
3a **4a** **5a**

Figure 5. Ball and stick representations of dyotropic transformation of *trans*-1,2-dibromocyclohexane, **3a**. All structures correspond to fully optimized B3LYP/LANL2DZ and 6-31+G(d) geometries. Bond lengths and angles are given in Å and degress, respectively. See Figure 2 caption for additional details.

Table 2. Selected bond lengths, activation energies and synchronicities for dyotropic rearrangements of compounds **3a**–**g**.

Entry	Compound	r(C–C) [Å]	E_a [kcal mol^{-1}]	S_y [a.u.]
1	**4a**, $X = X' = CH_2$	1.429	23.6	0.77
2	**4b**, $X = CH_2$; $X' = O$	1.437	17.1	0.74
3	**4c**, $X = X' = O$	1.442	15.1	0.73
4	**4d**, $X = CH_2$; $X' = S$	1.435	18.8	0.71
5	**4e**, $X = X' = S$	1.436	17.6	0.68
6	**4f**, $X = CH_2$; $X' = NH$	1.443	11.6	0.75
7	**4g**, $X = X' = NH$	1.450	5.05	0.81

found (Figure 7) validating the second-order pertubational analysis proposed for rearrangement in open chain compounds. Finally, in order to check our model, we computed the mixed-dyotropic reaction of 1-bromo-2-chlorocyclohexane (transition state **4h**, Figure 6). The E_a of this process is higher than the activation barrier of 1,2-dibromocyclohexane, which is in good agreement with the proposed dyotropically migratory aptitude of halogen atoms.[7b]



4b (C_1) **4c** (C_2) **4d** (C_1) **4e** (C_2)
4f (C_1) **4g** (C_2) **4h** (C_1)

Figure 6. Ball and stick representations of transitions structures **4b**–**g**. All structures correspond to fully optimized B3LYP/LANL2DZ and 6-31+G(d) geometries. Bond lengths and angles are given in Å and degrees, respectively.

Finally, we have also investigated the dyotropic rearrangements in polycyclic analogues of these 1,2-dibromocyclohexanes. The selected structures, which can be considered as models for steroid systems, are depicted in Scheme 6.

Conversion of dibromide **6** into its *cis* diastereomer **8** involves the isomerization of a *trans*-4a-methyldecalin to its *cis* diastereomer (Figure 8). According to our results, this process is favored thermodynamically, provided that decalin **8′** converts into **8**, in which both bromine atoms occupy equatorial positions, the methyl group being axial. It is interesting to note that in 4a-methyldecalin itself the *cis* isomer is found experimentally to be 0.550 ± 0.28 kcal mol^{-1} less stable than its *trans*-analogue.[20] Therefore, the two equatorial bromines override this energy difference in favor to the *cis*-decalin **8**. The saddle point **7** that connects **6** and **8′** local minima is calculated to lie about 16 kcal mol^{-1} above **6**, a value lower than that obtained for the monocyclic analogue **3a**. The synchronicity value obtained (Figure 8) is also similar to that found for the cyclohexane series (see Table 2).

The cyclopentanoperhydrophenantrene derivatives **9** and **11** are interconverted in transition-state structure **10**. This reaction is a very close analogue to the processes studied by Winstein[5] and Barton[6] (see Scheme 2). Our calculations (Figure 9) indicate that the activation barrier and the synchronicity values are very similar to those found for the previous reaction. In this case, however, compound **11′** is more destabilized with respect to its conformer **11**. The destabilization in **11′** arises from the twist conformation of the A,B rings of the steroid scaffold imposed by the C,D rings of the 3*a*-methyl-*trans*-hydrindane subunit (Figure 9), a conformational constraint which is not present in **8′**. Our calculations predict the exothermicity of this reaction in complete agreement with the experimental findings.[5,6] Finally, it is worthy to note that the computed NBO charges for the bromine atoms in saddle points **7** and **10**, and the S_y values of the corresponding reactions indicate that the dyotropic reactions take place through highly synchronous symmetry-allowed mechanisms. Again, both migrating bromine atoms are nearly equivalent in these complex

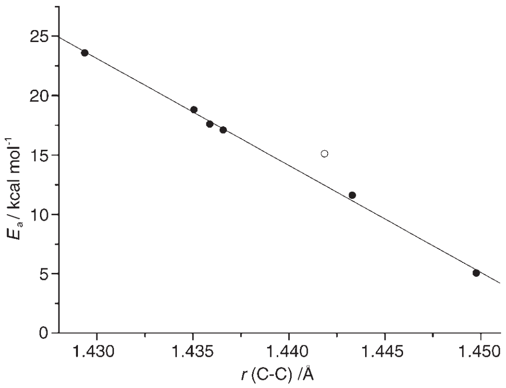
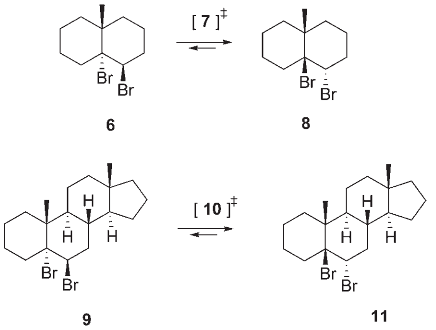


Figure 7. Plot of the activation energies (E_a) versus the C–C bond lengths of the transition states **4a–g**.



Scheme 6.

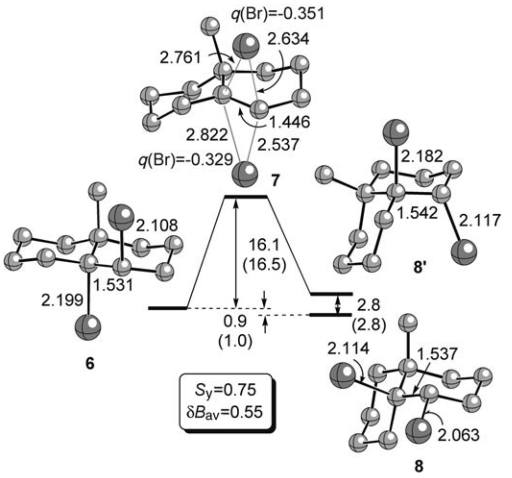


Figure 8. B3LYP/6-31G* and LANL2DZ optimized structures of **6**, **7**, **8** and **8′** (Scheme 6). Hydrogen atoms have been omitted for clarity. Numbers adjacent to the arrows are the energy barriers (which include zero-point vibrational energy corrections and are given in kcal mol^{-1}) and free energy barriers (in parentheses and computed at 298 K). q values refer to the respective NBO charges in a.u.

asymmetric systems. These results matched the geometries postulated by Winstein[5] and Barton[6] in their pioneering works.

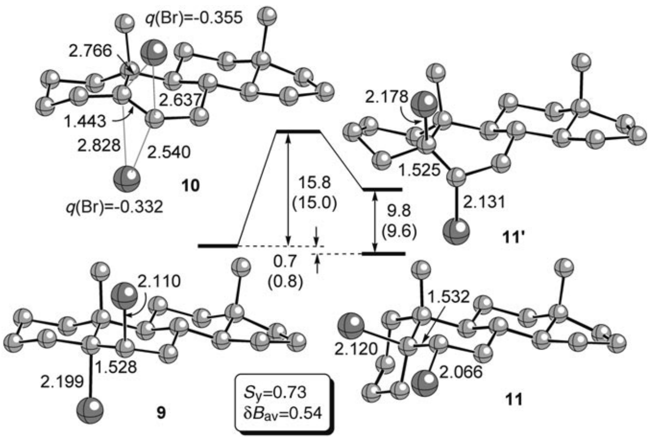


Figure 9. B3LYP/6-31G* and LANL2DZ optimized structures of **9**, **10**, **11** and **11′** (Scheme 6). See the caption of Figure 8 for additional details.

Conclusion

The effects of different substituents on type I-dyotropic rearrangements have been studied by means of DFT calculations. There are clear correlations between the donor ability of the heteroatom bonded to the reactive system (measured by the σ_p), the C–C and the activation energies needed for the rearrangement. Higher values of σ_p result in lower E_a and longer C–C and C–Br bond lengths in the corresponding transition states. A model based on the second-order perturbational analysis for one ethylene unit with two apical bromine radicals accounts for all the computed results. π-Donating substituents induce a stabilizing two-electron interaction between a filled orbital of the substituent and the parent LUMO leading to a more stable transition states. This interaction provokes the elongation of the C–Br bonds and elongation of the C–C bond length of the static scaffold, as well as a contraction of the C–X bond length. Strikingly, the computed values of the synchronicity (S_y) are high in all the studied systems rendering 1,2-dyotropic reactions synchronous and mostly independent on the substituents.

Acknowledgements

Support for this work under grant CTQ2004-06250-C02-01/BQU (to M.A.S.), CTQ2004-0681/BQU (to F.P.C.) from the Ministerio de Ciencia y Tecnología (Spain), and the Euskal Herriko Unibertsitatea (9/UPV 00040.215–13548/2001) (to F.P.C.) are gratefully acknowledged.

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Received: December 5, 2005
Revised: February 21, 2006