

## 1,2-Carbon to Nitrogen Migrations. Part 2.<sup>1</sup> *Ab Initio* Study on the Rearrangement of ( $\alpha$ -Methylazo)alkyl Isocyanates

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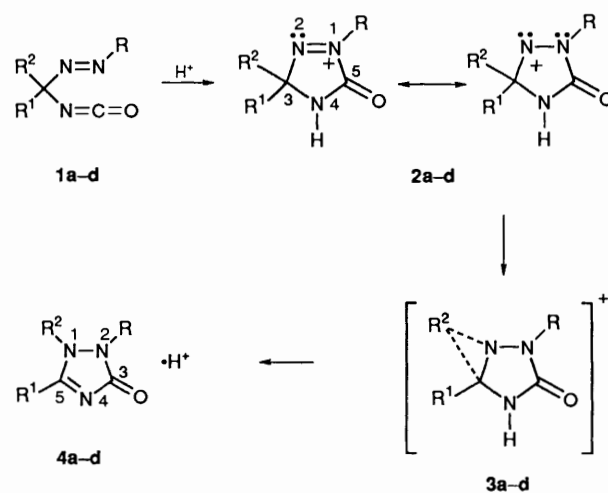
*Ab initio* molecular orbital calculations have been employed to study the rearrangement of ( $\alpha$ -methylazo)alkyl isocyanates to 1,2,5-trisubstituted 1,2-dihydro-1,2,4-triazol-3-ones. The migration of three different substituents (methyl, ethyl and isopropyl) has been investigated. Geometries of stationary points on the potential energy hypersurface were optimized at the HF/6-31G\* level of theory. Second order Moeller Plesset perturbation theory with the 6-31G\* basis set was applied in order to correct for correlation effects. Selected geometries were reoptimized at the MP2/6-31G\* level. HF/6-31G\*, MP2/6-31G\*//HF/6-31G\* and MP2/6-31G\* energies predict migratory aptitudes in the order isopropyl > ethyl > methyl. In the transition states, partial charges obtained from natural population analysis indicate strong electron deficiency at the nitrogen atom being the target for migration. The transition states show partial carbocation character of the migrating group with respect to charge distribution and geometry. An alternative reaction pathway, namely 1,2-shift of a methyl group to the adjacent nitrogen of the isocyanato function leading to formation of 2,4,5-trimethyl-2,4-dihydro-1,2,4-triazol-3-one, has been investigated, but can be excluded due to the much higher activation energy required.

Reactions involving 1,2-shift of a chemical group to an electron deficient atom play an important role in synthetic organic chemistry.<sup>2</sup> Nevertheless, little theoretical work has been performed on these types of reactions.<sup>3,4</sup> In organic textbooks and in the literature, 1,2-shifts to electron deficient atoms are often designated as nucleophilic and explained in terms of 'migration of the substituent with its electrons'.<sup>5</sup> Failure to observe racemization in the migrating substituent is ascribed to the fact that no free anion is formed.

Our previous calculations on the acid-induced rearrangement of ( $\alpha$ -alkylazo)alkyl isocyanates revealed partial carbocation character of the migrating alkyl in the transition states with respect to geometry and charge distribution.<sup>1</sup> In this work we present the results of *ab initio* calculations on the thermal rearrangement of ( $\alpha$ -alkylazo)alkyl isocyanates and compare them with the proton-catalysed reaction.

The acid-induced rearrangement of ( $\alpha$ -arylazo)alkyl isocyanates **1a** has proved a useful reaction for achieving the synthesis of 1,5-disubstituted 2-aryl-1,2-dihydro-1,2,4-triazol-3-ones **4a** in high yields (Scheme 1). One of the key steps in the overall reaction sequence is the proton-catalysed ring closure of the geminal functional groups of **1a**, leading to the formation of a diazenium functionality in the 3,3-disubstituted 1-aryl-1,2,4-triazolium salts **2a**. By 1,2-migration of a substituent to N2, the latter compounds rearrange under mild conditions to salts of 1,2,4-triazol-3-ones **4a**. Given two different substituents ( $R^1 \neq R^2$ ) in **2a**, migration takes place with exclusive selectivity in favour of the higher substituted carbon. *Ab initio* calculations on 1-methyl substituted triazolium salts **2b-d** revealed a significant electron deficiency at N2, which provides the basis for a subsequent 1,2-shift of a substituent *via* a three-centre transition state **3b-d** to this electron deficient atom.<sup>1</sup> Additionally, the migrating groups were shown to exhibit partial carbocation character in the transition states. According to these calculations, migratory aptitudes of different substituents parallel the stability of their respective carbocations.

The acid-induced rearrangement is not the only route for transformation of ( $\alpha$ -arylazo)alkyl isocyanates **1a** to 1,2,4-triazol-3-ones **4a**. Some of compounds **1a** were reported to

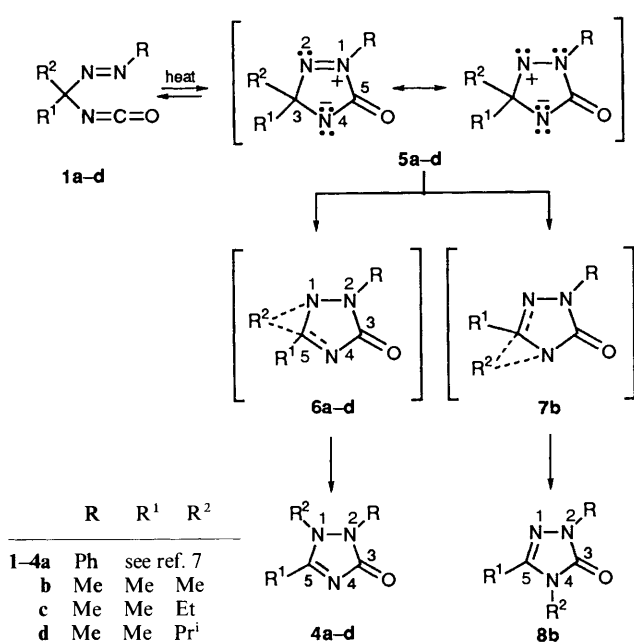


	R	R <sup>1</sup>	R <sup>2</sup>
1-4a	Ar	see ref.6	
b	Me	Me	Me
c	Me	Me	Et
d	Me	Me	Pr <sup>i</sup>

Scheme 1

convert directly into heterocycles **4a** upon heating (Scheme 2).<sup>7</sup> An exact explanation for the reaction mechanism has not been given, but a strongly polarized intermediate **5a**, representing a valence isomer of the starting material **1a**, was proposed on the reaction pathway **1a**→**4a**.<sup>6a</sup> Nevertheless, no chemical or spectroscopic evidence for the discrete formation of **5a** has been given. A systematic investigation of the thermal induced rearrangement of isocyanates **1a** to triazoles **4a** has not as yet been carried out. However, the few examples reported indicate similar selectivities for migration compared with the acid-induced reaction path.

In order to gain a deeper insight into the mechanism of the



Scheme 2

thermal rearrangement, two questions were of particular importance: (i) does an intermediate **5** exist on the potential energy hypersurface of the reaction and (ii) is there a possibility for 1,2-rearrangement of isocyanates **1** to 2,4,5-trisubstituted 2,4-dihydro-1,2,4-triazol-3-ones **8** via migration of a substituent to the nitrogen of the isocyanate function?

Whereas our previous calculations were performed on a system with an overall charge of +1 (au), the present investigation of the thermal induced rearrangement of ( $\alpha$ -methylazo)alkyl isocyanates deals with neutral molecules, thus providing the opportunity to compare the extent of polarization and associated effects in both systems, in particular at the atoms directly involved in 1,2-migration.

In summary, the points of major interest addressed in this theoretical study are: (i) investigation of the potential energy hypersurface in order to locate a minimum corresponding to structure **5**; (ii) examination of the possibility for rearrangement of isocyanates **1** to 2,4,5-trisubstituted 2,4-dihydro-1,2,4-triazol-3-ones **8** and comparison with the rearrangement **1**→**4**; (iii) the nature of the transition states **6** and **7** with respect to geometry and charge distribution; (iv) determination of activation energies and prediction of migratory aptitudes of different substituents R<sup>2</sup> in the rearrangement **1**→**4**; (v) a comparison of these values with the calculations on the acid-induced reaction **2**→**4**.<sup>1</sup>

The calculations were performed on a system with R = Me in order to save computational time, although rearrangements of ( $\alpha$ -methylazo)alkyl isocyanates have not yet been performed experimentally. The 1,2-migration of a methyl group to the adjacent isocyanato nitrogen (R<sup>2</sup> = R<sup>1</sup> = Me, **1b**→**8b**) and the 1,2-shifts of three different substituents to the diazene nitrogen (R<sup>2</sup> = Me, Et, Pr<sup>i</sup>; R<sup>1</sup> = Me, **1b-d**→**4b-d**) were examined.

### Calculations

The calculations were carried out on IBM RS6000/550- and IRIS Power Series 210-workstations with the GAUSSIAN92 quantum chemical program<sup>8</sup> and on a Convex 220 computer with the GAUSSIAN90 program.<sup>9</sup> Geometries of the stationary points were fully optimized without symmetry constraints at the single determinantal Hartree-Fock level of theory using the split-valence d-polarization 6-31G\*<sup>10</sup> basis set. Harmonic

vibrational frequencies<sup>11</sup> were computed at the HF/6-31G\* level in order to characterize stationary points (minima and first order saddle points, the latter having exactly one imaginary frequency) and to estimate the zero-point energy ( $E_z$ ) contributions to the relative energies between stationary points.<sup>12</sup> Atomic electron populations were calculated by means of the natural population analysis.<sup>13</sup> To correct for correlation effects, single point calculations applying frozen core second order Moeller-Plesset perturbation theory<sup>14</sup> (MP2/6-31G\*\*/HF/6-31G\*) were performed on the 6-31G\* optimized geometries. MP2/6-31G\* optimizations were started with the HF/6-31G\* force constants. Two-configuration SCF calculations (TCSCF, with minimal active space including two electrons and two orbitals) were carried out on the HF/6-31G\* optimized transition states in order to determine the possible biradical character of these structures. TCSCF is recognized as being the simplest theoretical approach for obtaining a quantitative measure of how close the wave function is to complete biradical character as indicated by the natural orbital occupation numbers  $N(\Phi)$  and  $N(\Phi^*)$ .<sup>15</sup> For triplet states both orbitals would be singly occupied [*i.e.*  $N(\Phi) = N(\Phi^*) = 1$ ; whereas  $N(\Phi) = 2$  and  $N(\Phi^*) = 0$  for singlet states]. In this study  $N(\Phi)$  was found to be higher than 1.90 [ $N(\Phi^*) < 0.10$ ] for all transition states, therefore justifying their treatment as singlets with the RHF-formalism.

### Results and Discussion

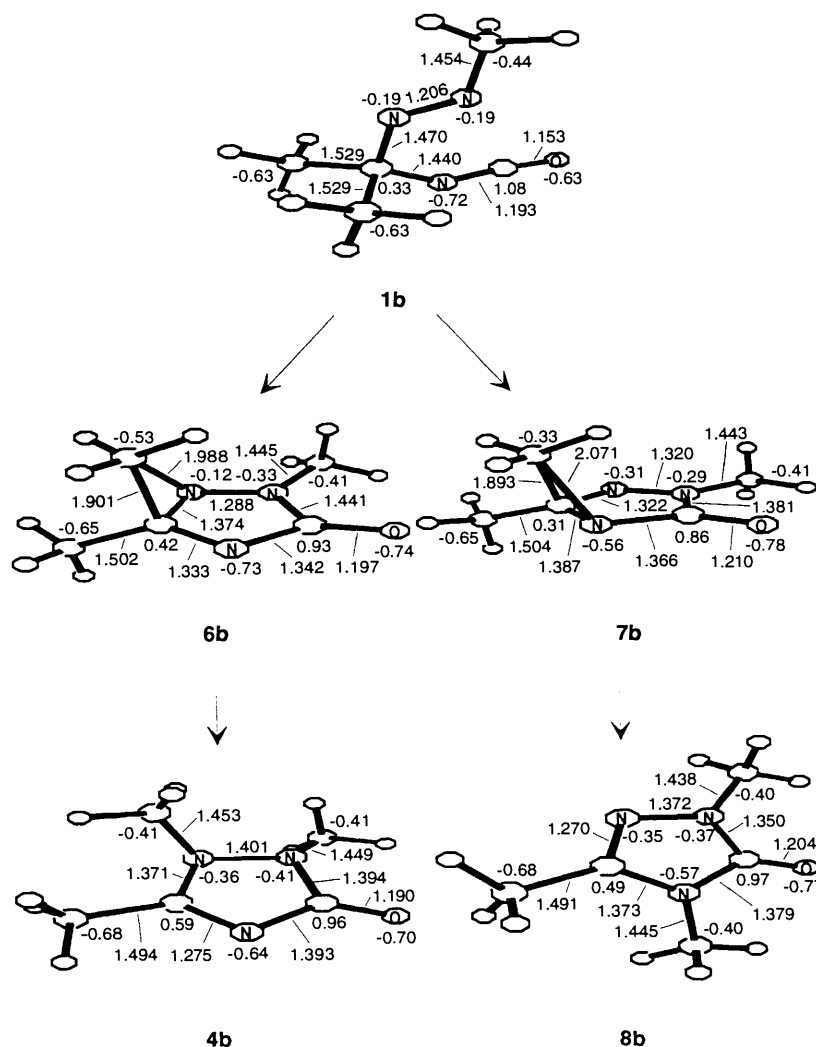
One important point for elucidation of the reaction mechanism for rearrangement of ( $\alpha$ -methylazo)alkyl isocyanates was to clarify the role of the hypothetical intermediate **5**, representing a valence isomer of the corresponding isocyanate **1**. Although extensive attempts were made in order to locate a local energy minimum resembling structure **5b**, no such minimum was found at the HF/6-31G\* level; each full geometry optimization starting with a geometry such as **5b** converged to the corresponding isocyanate. Optimizations with various fixed N1-C5 distances (range: 1.4–2.6 Å, step size: 0.2 Å) only resulted in increased energies in parallel with shorter N1-C5 distances (+95.8 kJ mol<sup>-1</sup> compared with structure **1b**, N1-C5: 1.4 Å). It is therefore unlikely that a local energy minimum corresponding to a geometry similar to **5b** would be found, even with the application of higher levels of theory.

Fig. 1 shows the HF/6-31G\* optimized geometries of the educt, the transition states and the products for the reaction pathways of 1,2-rearrangement of a methyl group to both of the adjacent nitrogen atoms in ( $\alpha$ -methylazo)alkyl isocyanate **1b**. On the basis of the calculated activation energies for the two pathways, migration to the diazene nitrogen (**1b**→**4b**) is favoured by 47.9 kJ mol<sup>-1</sup> (MP2/6-31G\*\*/HF/6-31G\*, Tables 1 and 2). Therefore, 1,2-shift of a carbon substituent to the nitrogen of the isocyanate functionality (**1b**→**8b**) can be excluded. Although the reaction energy is calculated to be negative for both pathways, 2,4,5-trimethyl-2,4-dihydro-1,2,4-triazol-3-one **8b** is found to be significantly (67.7 kJ mol<sup>-1</sup>, HF/6-31G\*) more stable than its isomer 1,2,5-trimethyl-2,4-dihydro-1,2,4-triazol-3-one **4b**. Hence, due to a large difference in activation energies, the thermodynamically less stable product is formed. The calculations reveal complete planarity for triazol-3-one **8b**, the thermodynamically more stable isomer; the torsional angles between the heavy atoms being 0° or 180° ± 0.1°. In contrast, the dihedral angles between the atoms of the azole ring in **4b** deviate from planarity by up to 10° and the two methyl substituents at N1 and N2 are bent out of the azole plane in opposite directions, by approximately 35°.

For 1,2-migration of the ethyl and isopropyl group to the adjacent diazene nitrogen, three different reactant and transition state structures were optimized (**1c**, **1c'**, **1c''** and **6c**,

**Table 1** Electronic energies (hartrees) and zero-point energies of the optimized structures

Structure	HF/6-31G*	MP2/6-31G**//HF/6-31G*	MP2/6-31G*	$E_z$ /kJ mol <sup>-1</sup>
<b>1b</b>	-432.752 106	-434.051 123	-434.060 253	435.5
<b>6b</b>	-432.672 658	-433.994 665	-434.000 022	432.5
<b>4b</b>	-432.774 510			
<b>7b</b>	-432.634 298	-433.976 331		432.2
<b>8b</b>	-432.800 294			
<b>1c</b>	-471.785 126	-473.216 729		519.3
<b>6c</b>	-471.706 517	-473.163 592		516.6
<b>1c'</b>	-471.784 176	-473.215 611		519.3
<b>6c'</b>	-471.709 374	-473.165 720		516.3
<b>1c''</b>	-471.786 190	-473.218 145	-473.227 655	519.2
<b>6c''</b>	-471.710 257	-473.168 462	-473.174 623	516.4
<b>1d</b>	-510.816 153	-512.383 191		601.7
<b>6d</b>	-510.742 960	-512.336 670		599.0
<b>1d'</b>	-510.818 035	-512.385 469		601.8
<b>6d'</b>	-510.741 132	-512.337 036		599.4
<b>1d''</b>	-510.816 961	-512.384 133	-512.393 893	601.8
<b>6d''</b>	-510.745 333	-512.340 315	-512.346 793	598.7

**Fig. 1** HF/6-31G\* optimized structures of the educt (**1b**), the transition states (**6b**, **7b**) and the products (**4b**, **8b**) for 1,2-migration of a methyl group to an adjacent nitrogen in ( $\alpha$ -methylazo)alkyl isocyanate **1b**. Bond lengths in Å, partial charges in au.

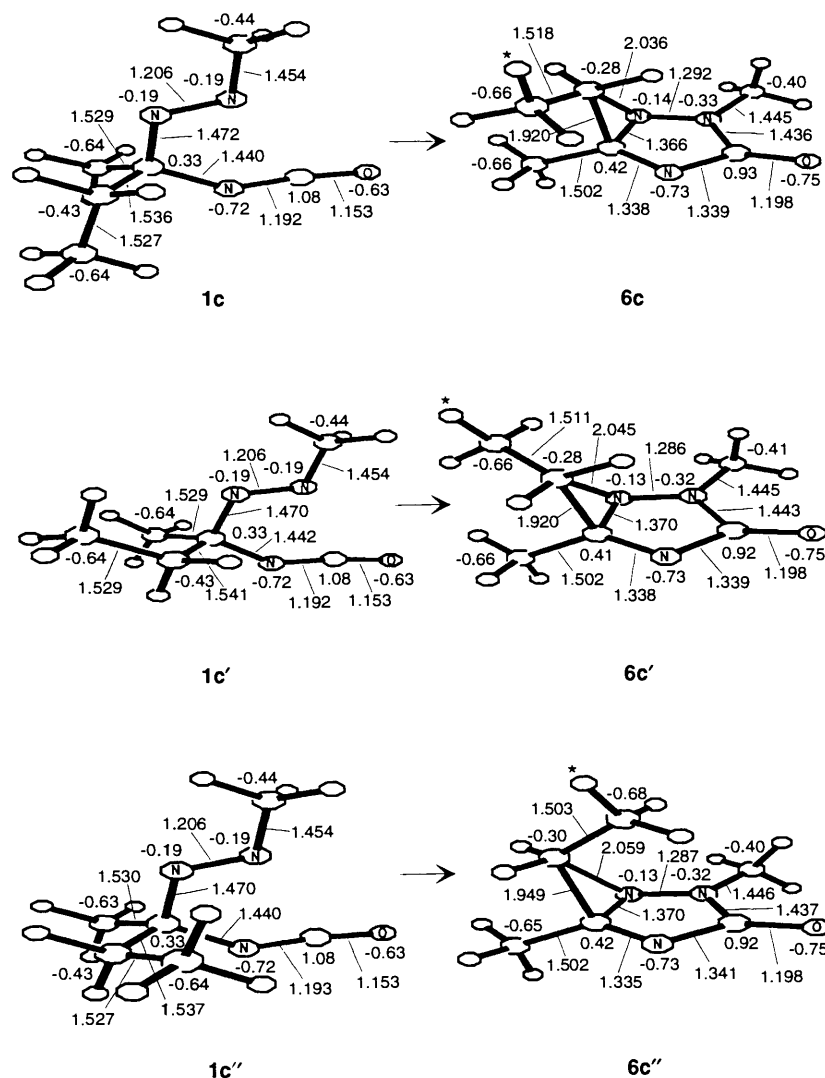
**6c'**, **6c''** for ethyl; **1d**, **1d'**, **1d''** and **6d**, **6d'**, **6d''** for isopropyl; Figs. 2 and 3), taking into account their thermodynamically favoured conformations. Intrinsic reaction coordinate (IRC) calculations<sup>16</sup> carried out with the STO-3G basis set<sup>17</sup> revealed that each of the transition states corresponds to exactly one educt conformer. In the transition states **6b**–**6d''**, bond formation

between N2 and C3 is complete and the atoms of the triazole ring adopt a product-like geometry. N1, the target for migration, is significantly more positive than the other nitrogen (N2) of the former diazene functionality. A similar polarization has already been observed in the transition states **3** for the acid-induced rearrangement of isocyanates **1**.<sup>1</sup>

**Table 2** Calculated activation and reaction energies (kJ mol<sup>-1</sup>)

	HF/6-31G* <sup>a</sup>	$\bar{E}_A^b$ HF/6-31G*	MP2/6-31G*//HF/6-31G* <sup>a</sup>	$\bar{E}_A^b$ MP2/6-31G*//HF/6-31G*	MP2/6-31G*
	<b>1b</b> → <b>6b</b>	205.7	205.7 (19.9)	145.3	145.3 (32.8)
<b>1c</b> → <b>6c</b>	203.8	194.3 (8.5)	136.9	128.0 (15.5)	139.3 (15.6)
<b>1c'</b> → <b>6c'</b>	193.5		128.0		
<b>1c''</b> → <b>6c''</b>	196.7		127.7		
<b>1d</b> → <b>6d</b>	189.5	185.8 (0)	119.4	112.5 (0)	123.7 (0)
<b>1d'</b> → <b>6d'</b>	199.7		124.9		
<b>1d''</b> → <b>6d''</b>	185.1		112.1		
<b>1b</b> → <b>7b</b>	306.2	306.2 (120.4)	193.2	193.2 (80.7)	
<b>1b</b> → <b>4b</b>	-58.9				
<b>1b</b> → <b>8b</b>	-126.6				

<sup>a</sup> Zero-point energies included for the activation energies. <sup>b</sup> Calculated from eqn. (1). Relative energies are given in parentheses.



**Fig. 2** HF/6-31G\* optimized structures of reactant conformers (**1c**, **1c'**, **1c''**) and the corresponding transition states (**6c**, **6c'**, **6c''**) for ethyl migration. Bond lengths in Å, partial charges in au.

As in the proton-catalysed reaction, the overall partial charge of the migrating substituent ( $\Sigma q_i$ ) is more positive in the transition states than in the reactants (Table 3). This is also indicated by the geometrical properties of the transition states: bond angles at the migrating carbon  $C_m$  are widened, indicating increased planarity for that group, and the  $C_m$ -C(methyl) distances are shorter than those in the educts (Table 3, Figs. 2 and 3). Each methyl group at  $C_m$  is orientated in such a way that the plane defined by one of its hydrogens (the corresponding hydrogen is marked by an asterisk in Figs. 2 and 3), the methyl

carbon (C) and  $C_m$  is almost perpendicular to the plane defined by the three atoms linked to  $C_m$  (two 2 hydrogens and one methyl carbon for ethyl; two methyl carbons and one hydrogen for isopropyl). The \*H-C bond is also slightly enlarged in comparison with the other H-C bonds in the methyl groups and bent towards  $C_m$  as indicated by a decreased \*H-C- $C_m$  angle. Such geometrical properties can be explained by hyperconjugation.<sup>18</sup> Bond shortening and planarity have also been observed in the X-ray structures of carbocations.<sup>19</sup>

In order to investigate the changes in charge distribution

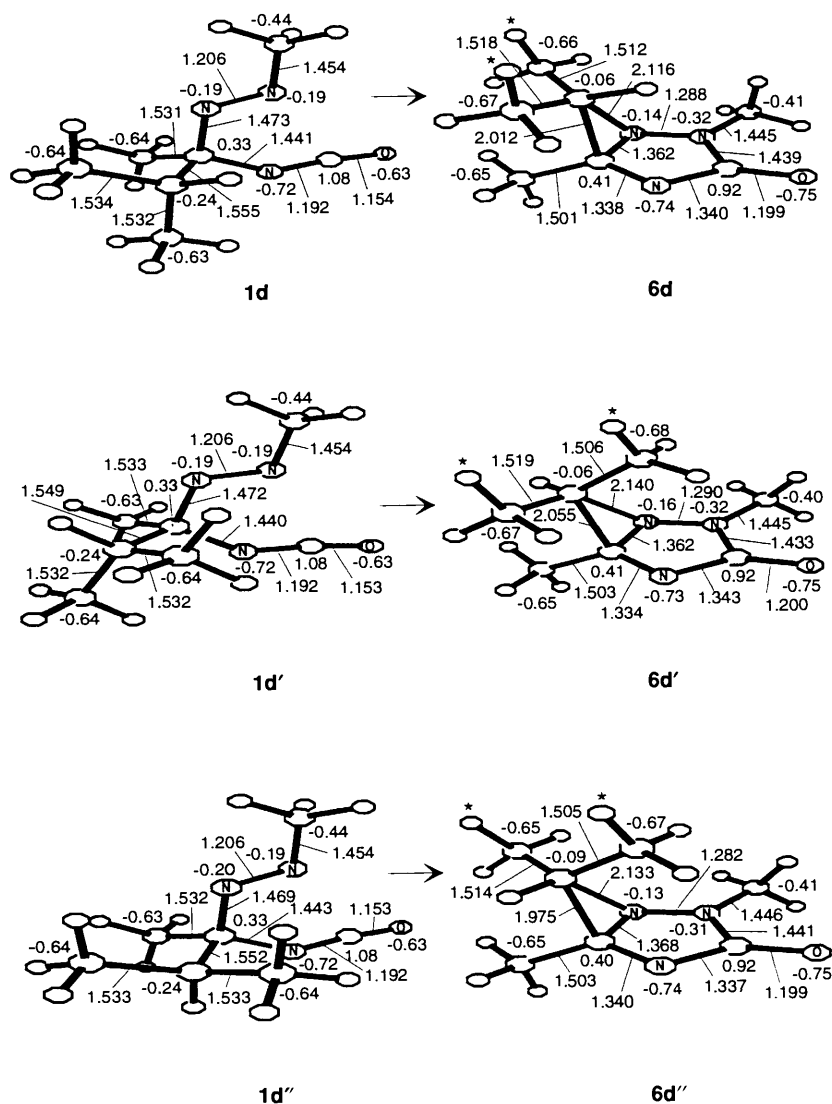


Fig. 3 HF/6-31G\* optimized structures of reactant conformers (**1d**, **1d'**, **1d''**) and the corresponding transition states (**6d**, **6d'**, **6d''**) for isopropyl migration. Bond lengths in Å, partial charges in au.

Table 3 Calculated properties of reactants and transition states for 1,2-rearrangement of a substituent to the adjacent nitrogen of the diazene functionality (average values)

	Reactant			Transition state		
	Me	Et	Pr <sup>i</sup>	Me	Et	Pr <sup>i</sup>
$\Sigma q_i^a$	0.06	0.05	0.05	0.20	0.24	0.27
H-C <sub>m</sub> -H <sup>b</sup>	108.9	107.0		112.3	110.8	
H-C <sub>m</sub> -C <sup>b,c</sup>		109.8	108.0		113.4	112.3
C-C <sub>m</sub> -C <sup>b,c</sup>			110.1			113.8
*H-C-C <sub>m</sub> <sup>b,c</sup>					107.9	107.9
H-C-C <sub>m</sub> <sup>b,c</sup>					112.0	112.0
*H-C <sup>c,d</sup>					1.088	1.088
H-C <sup>c,d</sup>					1.080	1.080

<sup>a</sup> Sum of partial charges in the migrating group (au). <sup>b</sup> Angles in degrees. <sup>c</sup> C denotes C(methyl) at C<sub>m</sub> in the migrating group. <sup>d</sup> Distances in Å.

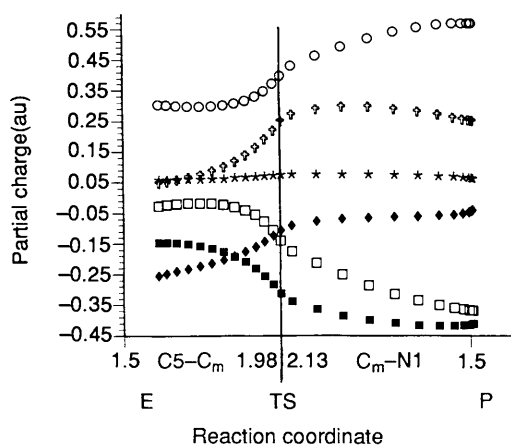
during the reaction in more detail, an IRC calculation at the HF/6-31G\* level was performed on transition state **6d'**. Twelve points were optimized stepping into the direction of the educt and the product, respectively. As already calculated for the acid-induced reaction, the charge of the entire migrating group (G)

becomes significantly more positive (Fig. 4). It reaches its maximum (+0.30 au) after the reaction has passed through the transition state. While the two nitrogens of the diazenium function become more negative, the positivation at C5, the starting point of the 1,2-shift, is significant. Other parts of the system, especially the methyl group at C5, do not display significant changes in charge distribution. In summary, the calculated carbocation character of the migrating groups is less pronounced in the thermal induced reaction than in the proton-catalysed rearrangement of isocyanates **1b-d**;<sup>1</sup> nevertheless it is a significant feature of the calculated transition states.

Determination of an average activation energy ( $\overline{E}_A$ , Table 2) for migration of the ethyl and isopropyl substituent was accomplished by substitution of the three respective activation energy values ( $\epsilon_j$ ) into a Boltzmann distribution and using the resulting values as weighting factors of the three  $\epsilon_j$  [eqn. (1)].<sup>1</sup>

$$\frac{N_j}{N} = \frac{e^{-\epsilon_j/kT}}{\sum_{j=1}^3 e^{-\epsilon_j/kT}} \quad \overline{E}_A = \sum_{j=1}^3 \frac{N_j}{N} \epsilon_j \quad (1)$$

The HF/6-31G\* activation energies reveal a clear distinction of the three substituents with respect to migratory aptitude in



**Fig. 4** Changes in partial charges during isopropyl migration ( $1d'' \rightarrow 6d'' \rightarrow$  product). E marks the educt, TS the transition state and P the product. The reaction coordinate corresponds to the C5-C<sub>m</sub> distance (Å) until the transition state is reached, in the second part the C<sub>m</sub>-N1 distance is displayed. The partial charge of the individual atoms are represented by (○), C5; (◆), C<sub>m</sub>; (□), N1; (■), N2; (▲), G; and (★), M; where G is the charge on the migrating substituent and M is the group charge of the methyl substituent at C5.

the expected order (isopropyl > ethyl > methyl). At the MP2/6-31G\*\*/HF/6-31G\* level, activation energies are much lower and display higher selectivity for migration of the substituents than at the HF/6-31G\* level.

In order to estimate the influence of electron correlation on energies and geometries, the structures **1b**, **6b**, **1c''**, **6c''**, **1d''** and **6d''** were reoptimized at the MP2/6-31G\* level of theory. The structural differences are small compared with the HF/6-31G\* optimized molecules. The most remarkable geometrical change is a decrease of the N-C-O angle from 171.5° (HF/6-31G\*) to 167° (MP2/6-31G\*) in the isocyanates **1b**, **1c''** and **1d''**. At both levels of theory, the bond angle is exceptionally small<sup>20</sup> and can be explained by repulsion between the diazene nitrogen and the carbon of the isocyanate function.<sup>21</sup> The activation energies are slightly higher than in the MP2/6-31G\*\*/HF/6-31G\* case, but the energy differences with respect to migration of the three different substituents remain approximately the same.

## Conclusions

*Ab initio* calculations at the HF/6-31G\*, MP2/6-31G\*\*/HF/6-31G\* and MP2/6-31G\* levels of theory predict relative reactivities of different alkyl substituents in the thermal rearrangement of ( $\alpha$ -methylazo)alkyl isocyanates in the order isopropyl > ethyl > methyl. For this series of substituents, the calculated activation energies are generally higher and the differences between them are smaller than calculated for the acid-induced rearrangement of isocyanates **1b-d**.<sup>1</sup> In the transition states, the nitrogen atom being the target for migration (N1) is significantly more positive than the other nitrogen (N2) of the former diazene functionality. The carbocation character of the migrating substituents in the corresponding transition states, as indicated by their formal charge and geometry, is less pronounced compared with the acid-induced reaction, but is still a distinct feature of these structures. This minor carbocation character results from the difference in the overall charge of the calculated molecules (+1 for the proton-catalysed reaction,<sup>1</sup> zero for the thermal rearrangement).

In conclusion, the magnitude of electron deficiency developed by the migrating alkyl group in the transition state, together with the ability of the system to stabilize this polarization, appear to determine the migratory aptitude and the degree of

selectivity in 1,2-migrations of alkyl substituents to electron deficient atoms.

An intermediate resembling structure **5b**, representing a valence isomer of the corresponding isocyanate, was not found. It can be concluded that the thermal rearrangement of ( $\alpha$ -methylazo)alkyl isocyanates takes place in a single kinetic step. The transition states reveal a substantial degree of asynchronicity with respect to bond breaking and formation. Considering these facts, the thermal rearrangement of ( $\alpha$ -methylazo)alkyl isocyanates represents a reaction which is concerted but not synchronous, *i.e.* a two-stage reaction.<sup>22</sup>

The activation energy for 1,2-migration of a methyl group to the adjacent nitrogen of the isocyanato functionality is calculated to be much higher than for 1,2-shift to the adjacent diazene nitrogen. Although the more stable product would be formed on the former reaction path, the probability of a rearrangement proceeding *via* this pathway can be excluded.

## Acknowledgements

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