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1,2-Shift of Carbon to Electron-Deficient Nitrogen Is Not a Nucleophilic Rearrangement. *Ab Initio* Study on a 1,2-Rearrangement in 1,2,4-Triazolium Salts

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Abstract: *Ab initio* molecular orbital calculations have been employed to study the unimolecular rearrangement of 3,3-disubstituted 1-methyl-5-oxo-4,5-dihydro-3*H*-1,2,4-triazolium cations to protonated 1,5-disubstituted 2-methyl-1,2-dihydro-1,2,4-triazol-3-ones. The 1,2-migration of three different substituents (methyl, ethyl, and isopropyl) has been investigated on the basis of a three-center transition-state model. 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 was applied with the 6-31G* basis set in order to correct for correlation effects. On the basis of HF/6-31G* and MP2/6-31G*//HF/6-31G* activation energies, migratory aptitudes are predicted in the order isopropyl $\gg$ ethyl $\gg$ methyl, which is in excellent agreement with experimental data reported for the rearrangement of 1-aryl-substituted 1,2,4-triazolium analogues. Partial charges obtained from the natural population analysis indicate strong electron deficiency at the nitrogen atom in the triazolium cations being the target for migration. The transition states show partial carbocation character of the migrating group with respect to charge distribution and geometry.

Introduction

Although reactions involving 1,2-shift of a chemical group to an electron-deficient atom play an important role in synthetic organic chemistry,[1] relatively little theoretical work has been done on this kind of reactions.[2,3] In the literature, such reactions are often referred to as nucleophilic rearrangements, implying that the "substituent moves with its electrons" and behaves like a carbanion.[4]

We present here the results of *ab initio* calculations on a 1,2-rearrangement in 1,2,4-triazolium salts, where the migrating substituents exhibit partial carbocation character during migration and in the transition states.

Schildknecht and Hatzmann first reported that α-(phenylazo)alkyl isocyanates (**1**) undergo a remarkable transformation upon treatment at elevated temperatures to give 1,5-disubstituted 2-phenyl-1,2-dihydro-1,2,4-triazol-3-ones (**4**) (Scheme 1, route A; R = phenyl; $R^1 = R^2 =$ alkyl).[5] In the course of this reaction, ring closure and 1,2-migration of an alkyl substituent is indicated by the structure of the products **4**, but the reaction mechanism has remained unclear so far.

More recently, it has been demonstrated that the conversion **1** $\rightarrow$ **4** is dramatically accelerated under acidic reaction conditions, and the reaction proceeds at room temperature or even below. This acid-induced rearrangement of α-(arylazo)alkyl isocyanates (**1**) has been valuable to achieve the synthesis of salts of 1,5-disubstituted 2-aryl-1,2-dihydro-1,2,4-triazol-3-ones (**4**) at high yields (Scheme 1, route B; R = aryl; $R^1 = R^2 =$ alkyl).[6] Upon addition of a strong proton acid (e.g., HBF_4) to a solution of the isocyanates **1** in Et_2O, intermediate 3,3-disubstituted 1-aryl-5-oxo-4,5-dihydro-3*H*-1,2,4-triazolium salts (**2**) are formed. Several representatives of the intermediates **2** could be isolated and have been characterized analytically. These highly reactive compounds **2** rearrange under mild conditions to salts of 1,2,4-triazol-3-ones **4**. One of the key steps in the overall reaction sequence is the acid-induced ring closure of the geminal functional groups of **1**, resulting in the formation of a diazenium function in which N2 is believed to exhibit substantial electron deficiency. Subsequently, 1,2-shift of a carbon substituent to this electron-deficient nitrogen takes place to give **4**. Given two different substituents ($R^1 \neq R^2$), migration takes place with exclusive selectivity according to the order isopropyl > ethyl > phenyl > methyl. Different substituents at the phenyl ring (R) influence the overall kinetics of reaction but not the selectivity for migration.[6a] If the carbon substituents R^1 and R^2 are part of a ring system, the

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(1) (a) Smith, P. A. S. In *Molecular Rearrangements*; de Mayo P., Ed.; Interscience: New York, 1963; Vols. 1 and 2. (b) Conley, R. T.; Ghosh, S. In *Mechanisms of Molecular Migrations*; Thyagarajan, J., Ed.; J. Wiley: New York, 1971; p 203. (c) Banthorpe, D. V. In *Chemistry of the Azido Group*; Patai, S., Ed.; Interscience: New York, 1971; p 397. (d) Plesnicar, B. In *Oxidation in Organic Chemistry*; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; p 254. (e) Brown, H. C.; Schleyer, P. v. R. *The Nonclassical Ion Problem*; Plenum Press: New York, 1977. (f) Krow, G. R. *Tetrahedron* **1981**, *37*, 1283. (g) Smith, P. A. S. *Org. React.* **1947**, *3*, 337. (h) Olah, G. A. *Acc. Chem. Res.* **1976**, *9*, 41. (i) Collins, C. J. *Q. Rev. Chem. Soc.* **1960**, *14*, 357. (j) Gawley, R. E. *Org. React.* **1987**, *35*, 1. (k) Hogeveen, H.; van Kruchten, E. M. G. A. *Top. Curr. Chem.* **1979**, *80*, 89. (l) Kirmse, W. *Top. Curr. Chem.* **1979**, *80*, 125. (m) Shubin, V. G. *Top. Curr. Chem.* **1984**, *115–117*, 267. (n) See also ref 4a.

(2) References 2 and 3 give an overview of the rare theoretical work on reactions involving 1,2-migration to electron-deficient atoms. For the migration of H, see: (a) Nguyen, M. T. *Chem. Phys. Lett.* **1985**, *117*, 290. (b) Nguyen, M. T. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1289. (c) Nguyen, M. T. *J. Chem. Soc., Chem. Commun.* **1987**, 342. (d) Hunt, P. A.; Rzepa, H. S. *J. Chem. Soc., Chem. Commun.* **1989**, 623. (e) Nakamura, K.; Osamura, Y. *J. Phys. Org. Chem.* **1990**, *3*, 737.

(3) For the migration of C, see: (a) Rajyaguru, I.; Rzepa, H. S. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1819. (b) Csizmadia, I. G.; Gunning, H. E.; Gosavi, R. K.; Strausz, O. P. *J. Am. Chem. Soc.* **1973**, *95*, 133. (c) Nakamura, K.; Osamura, Y. *Tetrahedron Lett.* **1990**, *31*, 251. (d) Carrupt, P.-A.; Vogel, P. *J. Phys. Org. Chem.* **1988**, *1*, 287. (e) Stoute, V. A.; Winnik, M. A.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1974**, *96*, 6388. (f) Nakamura, K.; Osamura, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9112.

(4) For example, see: (a) Krow, G. R. *Org. React.* **1993**, *43*, 251. (b) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; p 942. (c) Finar, I. L. *Chemistry*, 6th ed.; Longman: England, 1985; Vol. 1, p 146. (d) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 4th ed.; Allyn & Brown, Inc.: Boston, 1983. (e) Hudlicky, M. *Oxidations in Organic Chemistry*; ACS Monograph; American Chemical Society: Washington, DC, 1990; p 186.

(5) Schildknecht, H.; Hatzmann, G. *Angew. Chem.* **1969**, *81*, 469; *Angew Chem., Int. Ed. Engl.* **1969**, *8*, 456.

(6) (a) Gstach, H.; Seil, P. *Synthesis* **1990**, 803. (b) Gstach, H.; Seil, P. *Synthesis* **1990**, 808. (c) Gstach, H.; Seil, P. *Synthesis* **1990**, 1048.

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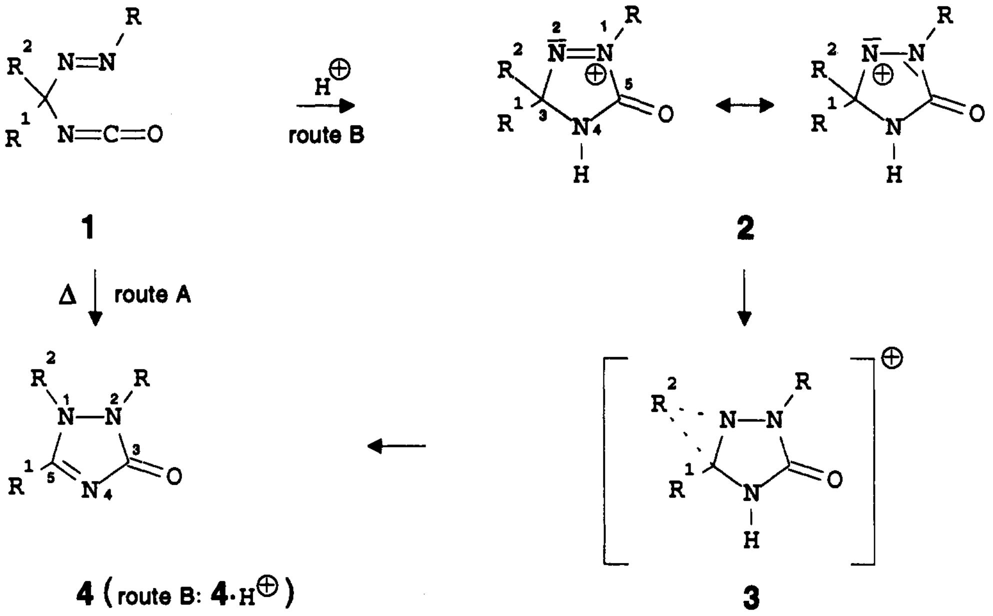
Scheme 1



rearrangement takes place with ring enlargement and insertion of the nitrogen atom into the carbon skeleton,[6b,c] thus demonstrating the broad synthetic scope of this reaction. Recently, a closely related rearrangement of 1,3,3-trisubstituted 3*H*-1,2,4-triazolium salts to 1,2,3-trisubstituted 1*H*-1,2,4-triazolium salts has been reported by Jochims et al.[7]

The present theoretical investigation of the rearrangement in triazolium salts **2** was initiated for several reasons. (1) The reaction is a rare example of a carbon-to-nitrogen rearrangement involving a diazenium functionality. (2) The diazenium group is not only present in the respective transition state but also already a feature of the reactants **2**; for one of the latter, an X-ray structure has already been reported.[8] (3) The reaction is a good model for studying the migration of a substituent to an electron-deficient nitrogen for two reasons. First, the triazolium salts are rather stable structures. This implies that no additional questions about the influence of a potential leaving group and/or the mechanism of the reaction (e.g., pinacol rearrangement: stepwise versus concerted mechanism) have to be addressed. Second, due to the geometry of the triazolium ions, both substituents competing for rearrangement have *a priori* the same chance to migrate.

By investigating the mechanism of this rearrangement, a deeper insight into the general characteristics of 1,2-migrations of carbon substituents to electron-deficient nitrogen atoms can be gained, and the results of the calculations can be compared with already available experimental data.

Several aspects of the reaction sequence are of particular interest, including the charge distribution in triazolium ions **2**, the origin of the high selectivity for migration, and the nature of the transition states **3** with respect to geometry and electron distribution.

One useful tool for analyzing reaction mechanisms is the assignment of atomic charges (atomic electron populations). This gives a measure of the bond polarization and is helpful in characterizing the shifts in electron density during chemical transformations. Neglecting the fact that covalent systems involve shared electron density, an arbitrary partitioning scheme must be applied to define these atomic populations. Because Mulliken populations have been criticized often, particularily for their basis set dependency,[9] we focused on the natural population analysis,[10] where partitioning is done in terms of localized orbitals. As it is *per se* problematic to represent molecules by atomic charges, thus exaggerating an ionic character of the bonds, we did not monitor only individual atomic populations but assigned the charges for entire chemical groups.

In the theoretical study presented here, the calculations were performed on a system with a methyl substituent at N1 in order to save computational time. The migration of three different substituents (R^2 = methyl, ethyl, and isopropyl; $R = R^1$ = methyl) was investigated for the reaction **2** → **4** using a three-center transition-state model for 1,2-shift of the migrating group.

Calculations

The calculations were carried out on IBM RS6000/550 and IRIS Power Series 210 workstations with the GAUSSIAN92 quantum chemical program[11] and on a Convex 220 computer with the GAUSSIAN90 program.[12] Geometries of the stationary points were fully optimized without symmetry constraints at the single determinantal Hartree–Fock level of theory using a split-valence d-polarization (6-31G*)[13] Harmonic vibrational frequencies[14] were computed 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 (ZPE) contributions to the relative energies between stationary points.[15] Atomic electron populations were calculated by means of the natural population[10] and the Mulliken population analysis[16] implemented in the GAUSSIAN programs. The charges used throughout this paper result from the natural

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[7] Wang, Q.; Jochims, J. C.; Koehlbrandt, S.; Dahlenburg, L.; Al-Talib, M.; Hamed, A.; Ismail, A. E. H. *Synthesis* **1992**, 710.

[8] Gstach, H.; Seil, P.; Schantl, J. G.; Gieren, A.; Huebner, T.; Wu, J. *Angew. Chem.* **1986**, *98*, 1111; *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 1132.

[9] For example, see: Reed, A. E.; Weinhold, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3586.

[10] (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Glendering, E. D.; Reed, A. E.; Carpenter, E.; Weinhold, F. *NBO*, Version 3.1.

[11] Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresmann, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian92*, Revision C; Gaussian, Inc.: Pittsburg, PA, 1992.

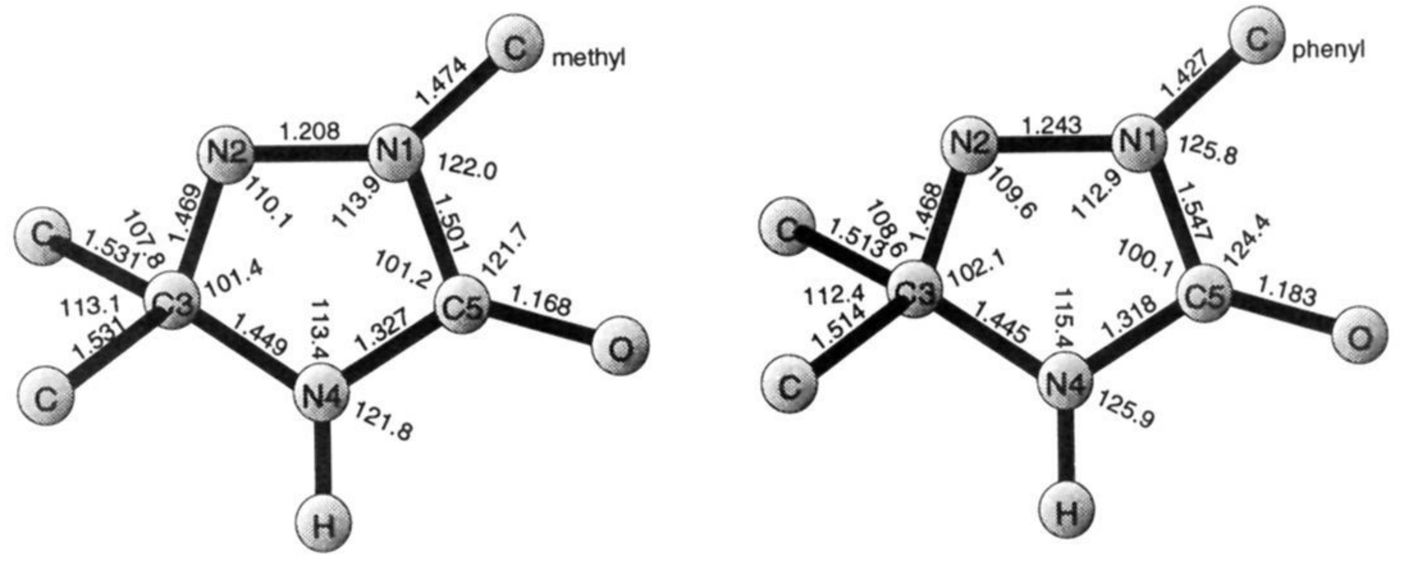
[12] Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresmann, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian90*, Revision H; Gaussian, Inc.: Pittsburg, PA, 1990.

[13] (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. In *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

[14] Mezey, P. G. In *Potential Energy Hypersurfaces*; Elsevier: New York, 1987.

[15] Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1981**, *15*, 269.

[16] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833; 1841; 2338; 2343.



5 **5'**

Figure 1. Geometrical comparison between the HF/6-31G* optimized geometry of **5** (1-methyl) and the X-ray structure of **5'** (1-phenyl). Bond lengths in angstroms; angles in degrees.

Table 1. Calculated Properties of Reactants and Transition States (Average Values)

	reactants			transition states		
	methyl	ethyl	isopropyl	methyl	ethyl	isopropyl
Σq_i[a]	0.12 (0.21)	0.12 (0.22)	0.12 (0.22)	0.36 (0.39)	0.45 (0.46)	0.53 (0.52)
q_{C_m}[b]	−0.65 (−0.47)	−0.45 (−0.30)	−0.25 (−0.16)	−0.44 (−0.44)	−0.17 (−0.26)	+0.09 (−0.08)
C_m–N2[c]				0	0.14	0.35
C_m–C3[c]				0	0.10	0.19
H–C_m–H[d]	108.9	107.0		113.6	112.9	
H–C_m–C[d,f]		110.2	108.3		115.8	115.0
C–C_m–C[d,f]			107.8			117.0
*H–C–C_m[d,f]					105.6	105.8
H–C–C_m[d,f]					112.9	112.7
*H–C[e,f]					1.089	1.089
H–C[e,f]					1.081	1.080

[a] Sum of partial charges in the migrating group (au; Mulliken charges in parentheses). [b] Partial charge at the migrating atom C_m (au; Mulliken charges in parentheses). [c] Interatomic distances relative to transition state **6** (Å). [d] Angles in degrees. [e] Distances in angstroms. [f] C denotes C(methyl) at C_m in the migrating group.

population analysis. In the text, Mulliken charges are given in parentheses. To correct for correlation effects, single-point calculations applying frozen core second-order Moeller–Plesset perturbation theory (MP2)[17] were performed with the HF/6-31G* optimized geometries. Two-configuration SCF calculations (TCSCF, with minimal active space including two electrons and two orbitals) were done on the optimized transition states in order to determine the possible biradical character of these structures. TCSCF is recognized to be the simplest theoretical approach to obtain a direct quantitative measure of how close the wave function is to complete biradical character as indicated by the natural orbital occupation numbers $N(\phi)$ and $N(\phi^*)$.[18] 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

A geometrical comparison between the 6-31G* optimized geometry of the 1,3,3-trimethyl-5-oxo-4,5-dihydro-3*H*-1,2,4-triazolium ion (**5**)[19] and the X-ray structure of its 1-phenyl-substituted analogue **5'**[8] is shown in Figure 1. Differences in bond lengths between the two structures are primarily located in bonds involving N1, due to different substitution at this atom in the two molecules. The calculated C5–O distance is 0.01 Å longer than that in the heterocumulene methyl isocyanate optimized with the same basis set[20] and is remarkably short. In general, bond lengths and angles are reproduced accurately by the calculations.

In the triazolium ions with two different substituents at C3, significant increases of 0.01 Å for the C3–CH_2CH_3 (**7**, **9**, and **11**) and 0.02 Å for the C3–$CH(CH_3)_2$ bond lengths (**13**, **15**, and **17**) are calculated (Figures 2 and 3; for atom numbering see Figure 1). The carbon of the ethyl or isopropyl group linked to C3 is more positive relative to the methyl carbon at C3. Moreover, the triazolium ions appear to be strongly polarized, as revealed by the partial charges (au) of +0.98 (+1.00) at C5 and −0.75 (−0.80) at N4. N2 bears a positive charge of +0.08 (−0.02), whereas N1 remains with a charge of −0.12 (−0.32) slightly negative. This indicates strong electron deficiency in the diazenium function, especially at N2, the target for migration.

Three different reactant and transition-state structures were optimized for ethyl (**7**, **9**, and **11** and **8**, **10**, and **12**) and for isopropyl migration (**13**, **15**, and **17** and **14**, **16**, and **18**), taking into account the thermodynamically favored conformations (Figures 2 and 3). Intrinsic reaction coordinate (IRC) calculations[21] at the STO-3G level[22] revealed that each of the transition states corresponds to exactly one educt conformer, as shown in Figures 2 and 3.

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(17) (a) Moeller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1976**, *10*, 1. (c) Szabo, A.; Ostlund, N. S. In *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Macmillan: New York, 1982.

(18) (a) Bender, C. F.; Schaefer, H. F., III; Franceschetti, D. R.; Allen, L. C. *J. Am. Chem. Soc.* **1972**, *94*, 6888. (b) Cossio, F. P.; Ugalde, J. M.; Lopez, X.; Lecea, B.; Palomo, C. *J. Am. Chem. Soc.* **1993**, *115*, 995.

(19) (a) Schantl, J. G.; Lanznaster, N.; Gstach, H. *Heterocycles* **1990**, *31*, 825. (b) Schantl, J. G.; Lanznaster, N.; Gstach, H. *Heterocycles* **1990**, *31*, 833.

(20) Kroemer, R. T., unpublished results.

(21) (a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(22) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

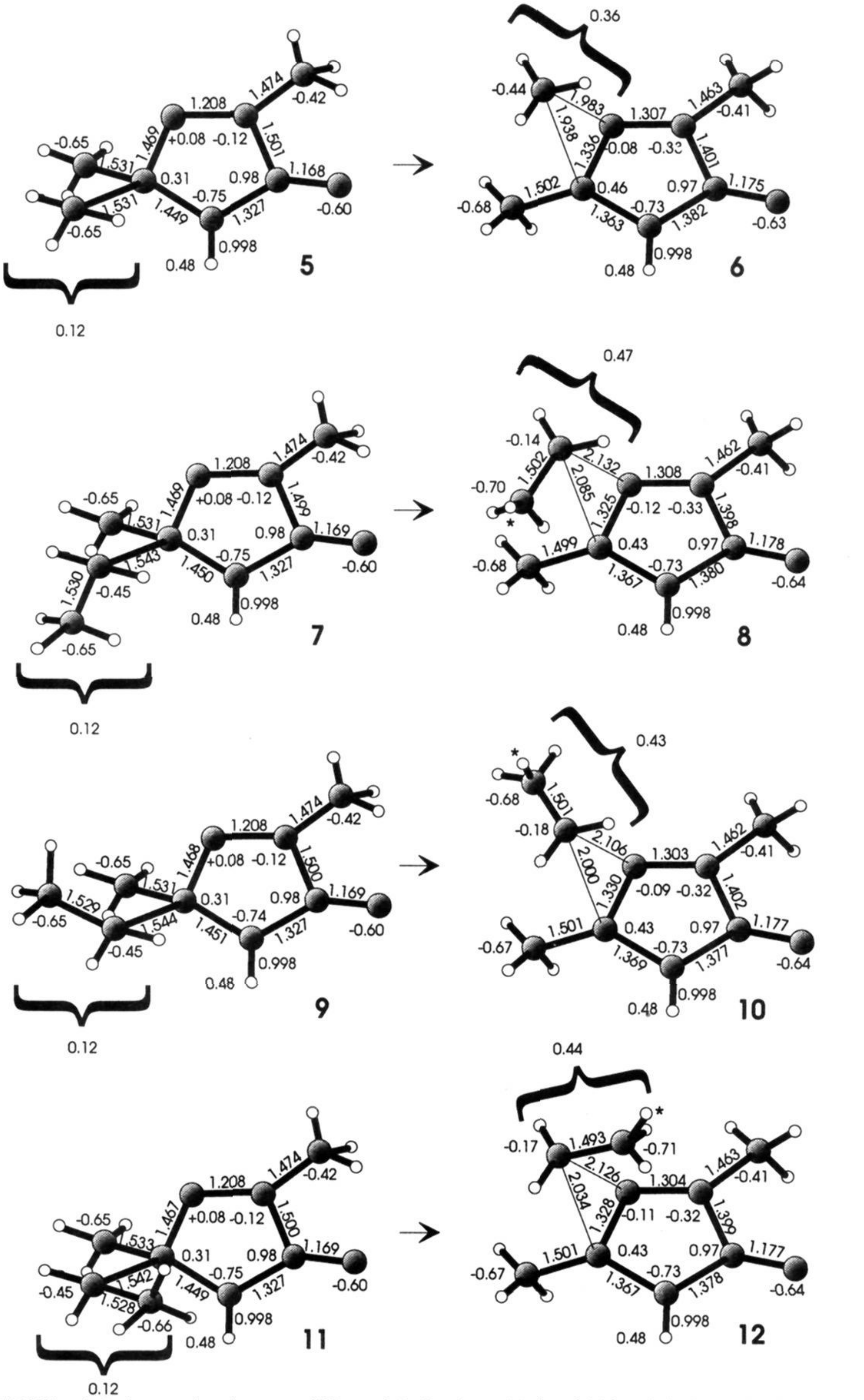

Figure 2. HF/6-31G* optimized geometries of reactants (**5** for methyl migration and **7**, **9**, and **11** for ethyl migration) and transition states (**6** and **8**, **10**, and **12**). Bond lengths in angstroms; partial charges and the group charges of the migrating substituents in atomic units.

In the transition states with higher substitution at the migrating carbon (C_m), an increase in the distances C_m–N2 and C_m–C3 is apparent (Table 1). The values of 1.938–2.371 Å for these distances lie within the expected range.[3] Several bond lengths in the azole ring have changed considerably, reflecting a more product-like geometry.[23] For instance, the N1–N2 distance is increased by 0.1 Å, while the C3–N4 bond length is shortened by 0.09 Å.

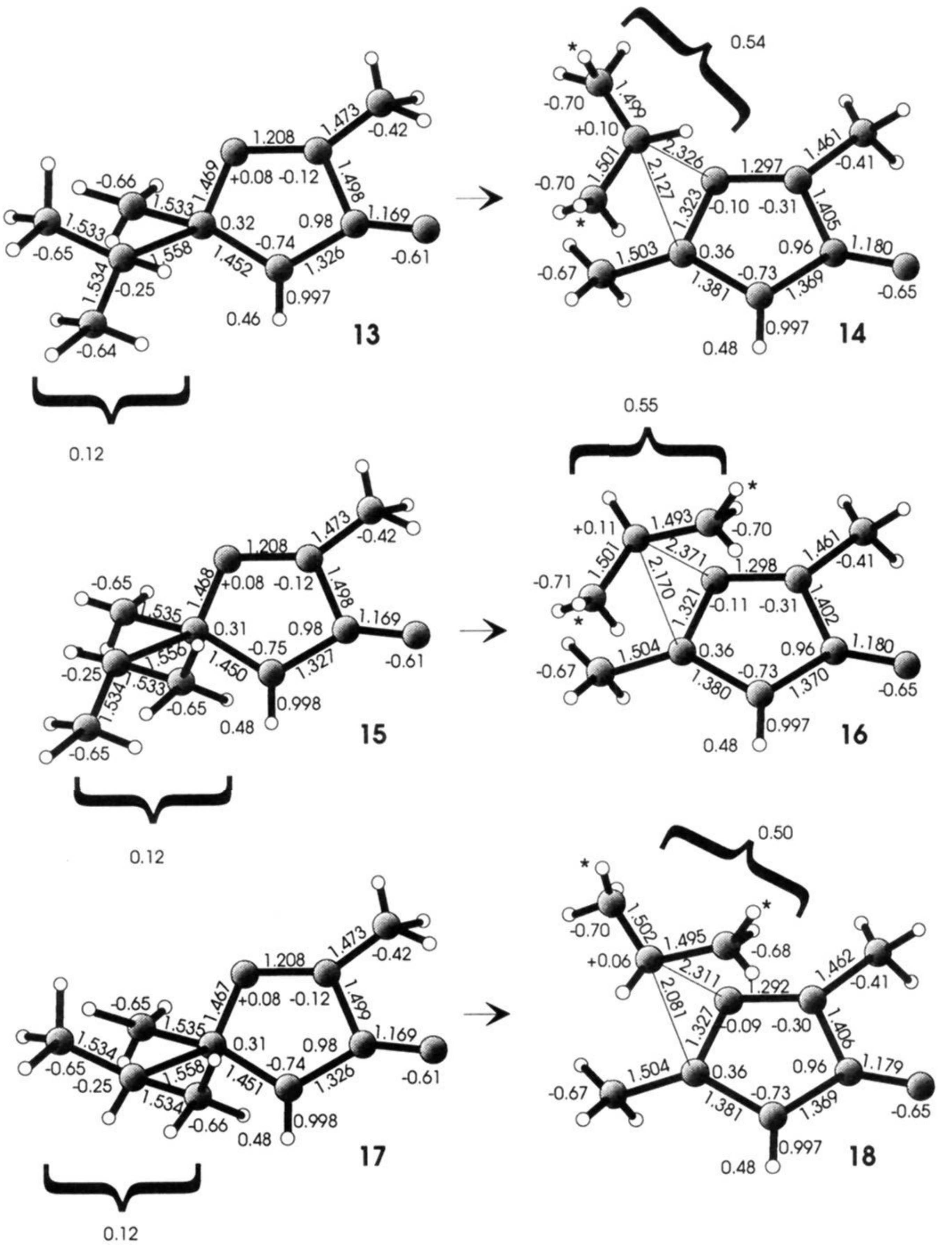

Figure 3. HF/6-31G* optimized geometries of reactants (**13**, **15**, and **17**) and transition states (**14**, **16**, and **18**) for isopropyl migration. Bond lengths in angstroms; partial charges and the group charge of isopropyl in atomic units.

A partial carbocation character of the migrating groups is indicated by two points, their geometry in the transition states and the changes of charge distribution in the system during migration.

(1) Bond angles at C_m in the transition states are widened, indicating increased planarity for the migrating group, and the C_m–C(methyl) distances are shorter than those in the educts by 0.03 Å (Table 1, Figures 2 and 3). Such geometrical properties are also observed in X-ray structures of carbocations.[24] 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 Figures 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 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 to the other H–C bonds in the methyl groups and bent toward $\mathbf{C_m}$, as indicated by a decrease in the *H–C–C_m angle (Table 1). These geometrical changes may be explained by hyperconjugation.[25]

(2) The overall partial charge of the migrating substituent as well as the charge at C_m is more positive in the transition states than in the educts (Table 1, Figures 2 and 3). For isopropyl migration, C_m is already positively charged in the corresponding transition states. In order to analyze the reaction mechanism more thoroughly, an IRC calculation at the HF/6-31G* level was performed on transition state **18** (isopropyl migration). Nine points were optimized stepping into the direction of the educt, 10 on the product side. For each of these points, the wave function

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(23) Ritchie, J. P. *J. Org. Chem.* **1989**, *54*, 3553.

(24) (a) Hollenstein, S.; Laube, T. *J. Am. Chem. Soc.* **1993**, *115*, 7240. (b) Laube, T. *Angew. Chem.* **1987**, *99*, 580; *Angew Chem., Int. Ed. Engl.* **1987**, *26*, 560. (c) Laube, T. *J. Am. Chem. Soc.* **1989**, *111*, 7240.

(25) (a) Sieber, S.; Buzek, P.; Schleyer, P. v. R.; Koch, W.; Carneiro, J. W. de M. *J. Am. Chem. Soc.* **1993**, *115*, 259. (b) Mareda, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1280. (c) Koch, W.; Liu, B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1989**, *111*, 3479.

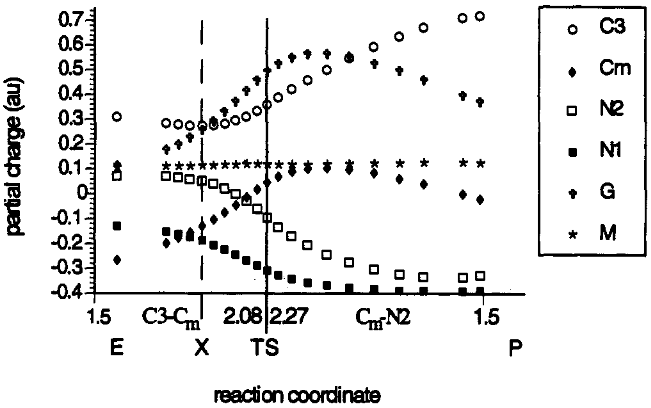

Figure 4. Changes in partial charges during isopropyl migration (**17** → **18** → product). E marks the educt, TS the transition state, and P the product. The reaction coordinate corresponds to the C3–C_m distance (Å) until the transition state is reached; in the second part the C_m–N2 distance is displayed. *G* is the charge of the entire migrating substituent, and *M* the group charge of the methyl substituent at C1. X marks the distance at which the development of a 3-center orbital (HOMO, in terms of localized orbitals) including C3, C_m, and N2 starts to be significant.

was analyzed in terms of localized orbitals,[26] and a natural population analysis was performed. The results are listed in Figure 4. In the initial phase of migration, C3 (the starting point of the 1,2-shift) becomes slightly more negative. This could be interpreted as charge transfer from C_m in order to satisfy the electronic demands of the neighbor atom of C3, the electron-deficient N2. When formation of a three-center orbital involving C3, C_m, and N2 starts to be significant (C_m–C3, 1.9 Å; C_m–N2, 2.4 Å), C3 becomes progressively more positive until it carries most of the positive charge in the molecule. The increasing positivity of C_m as well as that of the entire migrating group (G) reaches its maximum after the reaction has passed through the transition state. Especially in the first half of the reaction, the loss of charge is mostly apparent for the isopropyl group. The corresponding curve shows the steepest increase. The isopropyl group charge reaches its maximum of +0.57 (au) at a C_m–N2 distance of 2.1 Å (C_m–C3, 2.2 Å). At this point, the charge at C_m is also most positive (+0.12), and the distance between the two curves (for C_m and G) is highest. The two nitrogens of the diazenium function, especially N2 (the target for migration), become progressively more negative. Additionally, the charge at N2 changes its sign (from +0.08 in the educt to –0.32 near the product). Other parts of the system, especially the methyl group at C1 as well as N4, do not undergo significant changes in charge distribution.

Table 2 lists total energies of geometries **5**–**18** calculated at different levels of theory. Table 3 gives the activation energies calculated from Table 2. The determination of an average activation energy ($\bar{E}_A$) for migration of the ethyl and isopropyl substituents is based on the following facts and assumptions. (1) As indicated by the IRC calculations at the STO-3G level, each reactant conformer is transformed into the product via one corresponding transition state. (2) The rotational barrier for interconversion of the three respective conformationally different ethyl- or isopropyl-substituted triazolium cations (the reactants) amounts to approximately 5 kcal/mol at the HF/6-31G* level.[20] This is much lower than the activation energy of the reaction and gives an estimate for the energy required for transition from one reaction pathway to another. (3) Transformation to the product proceeds preferably via the minimum energy path.

The three respective activation energy values (ϵ_j) were then substituted into a Boltzmann distribution. The resulting values served as weighting factors of the three ϵ_j values in order to calculate the average activation energy $\bar{E}_A$ for the migration of the ethyl and isopropyl substituents (eq 1):

Table 2. Calculated Electronic Energies (hartrees) and Zero-Point Energies (kcal/mol) of Reactants and Transition States **5**–**18**

structure	6-31G*	MP2	ZPE
5	–433.119 715	–434.414 622	113.4
6	–433.063 477	–434.367 441	112.1
7	–472.154 683	–473.581 764	133.5
8	–472.103 057	–473.540 671	132.0
9	–472.154 207	–473.581 359	133.5
10	–472.106 248	–473.543 740	131.9
11	–472.155 272	–473.582 995	133.4
12	–472.107 142	–473.546 608	131.9
13	–511.188 244	–512.750 327	153.2
14	–511.146 287	–512.719 444	151.4
15	–511.188 886	–512.751 576	153.2
16	–511.145 278	–512.720 056	151.5
17	–511.187 999	–512.750 778	153.2
18	–511.148 571	–512.724 088	151.5

Table 3. Calculated Activation Energies (kcal/mol)

	6-31G* [a]	$\bar{E}_A$ 6-31G* [b]	MP2[a]	$\bar{E}_A$ MP2[b]
5 → **6**	33.9	33.9 (10.8)	28.3	28.3 (13.3)
7 → **8**	30.9	28.7 (5.6)	24.2	21.5 (6.5)
9 → **10**	28.6		22.1	
11 → **12**	28.7		21.3	
13 → **14**	24.6	23.1 (0)	17.6	15.0 (0)
15 → **16**	25.7		18.1	
17 → **18**	23.0		15.0	

[a] Zero-point energies included. [b] Calculated from eq 1. Relative energies are given in parentheses.

$$\frac{N_j}{N} = \frac{e^{-\epsilon_j/kT}}{\sum_{j=1}^{3} e^{-\epsilon_j/kT}} \qquad \bar{E}_A = \sum_{j=1}^{3} \frac{N_j}{N}\epsilon_j \tag{1}$$

The 6-31G* activation energies display a clear distinction of the three substituents with respect to migratory aptitude in agreement with experimental data reported on the 1-aryl-substituted triazolium salts.[6] At the MP2 level, calculated activation energies are lower. The differences in energy required for activation of 1,2-shift of the three alkyl substituents are slightly higher in the MP2 case compared to the 6-31G* energies (6.8 versus 5.2 kcal/mol comparing methyl with ethyl migration; 6.5 kcal/mol versus 5.6 kcal/mol comparing ethyl with isopropyl migration; Table 3).

The energy differences for 1,2-shift of the methyl, ethyl, and isopropyl groups obtained at HF/6-31G* and MP2/6-31G*//HF/6-31G* levels of theory guarantuee that, given two different substituents ($R^1 \neq R^2$) in triazolium salts **2**, only the product of migration of the higher substituted carbon should be observed experimentally.

Conclusions

The present results demonstrate the ability of *ab initio* calculations at the MP2/6-31G*//HF/6-31G* and HF/6-31G* levels to calculate relative reactivities for 1,2-migration of different alkyl substituents in 3,3-disubstituted 1-methyl-5-oxo-4,5-dihydro-3*H*-1,2,4-triazolium salts **2**; they predict complete selectivity for migration of the higher substituted carbon in agreement with experimental data reported on the rearrangement of 1-aryl-substituted analogues of **2**.[6]

The hypothesis that N2 in the 1-aryl-substituted triazolium salts **2** exhibits substantial electron deficiency[6c] has been supported by the charge distribution calculated for the 1-methyl-substituted structures **2**. This electron deficiency provides the basis for subsequent 1,2-shift of a carbon substituent to N2.

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[26] Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296.

The analysis of the partial carbocation character of the migrating substituent during migration and in the transition state is based on two facts. (1) The geometry of the migrating group in the transition state exhibits all the geometric features that have been observed in X-ray structures of and calculated for carbocations. (2) The partial charges of the migrating carbon as well as the group charge become significantly more positive. For the isopropyl shift, the migrating carbon appears to be even slightly positive.

Additionally, the migratory aptitude of the different substituents parallels clearly their ability to stabilize electron deficiency. We therefore raise the question of whether 1,2-rearrangements of carbon substituents to electron-deficient (hetero)atoms should continue to be described as nucleophilic.[4] An argument that racemization in such 1,2-shifts is not observed because the reaction is intramolecular and no "free anions" are formed should be avoided. According to our calculations, if the substituent becomes free during migration, a "free cation" should be formed. Anions do not emerge from bridged cations! On the other hand, these reactions should also not be called electrophilic. In our opinion, such a terminology is not valid for this type of reaction involving three-center transition states.

In the system investigated, relative reactivities appear to be mainly controlled by electronic factors. Accordingly, this rearrangement represents a valuable model for 1,2-shift of an alkyl group toward an electron-deficient nitrogen, but it should be considered that steric influences,[27] torsional strain,[28] and/or reaction conditions[29] can counteract or cancel these electronic effects in other reaction systems.

Taking into account that high selectivities and reasonable activation energies are predicted by theoretical calculations on the rearrangement in electron-donor (1-methyl)-substituted triazolium salts **2**, an experimental realization of this reaction should be feasible in analogy to the already described 1,2-shift in electron-acceptor (1-aryl)-substituted triazolium salts.

Furthermore, as is indicated by the remarkable charge distribution in the diazenium functionality, 1,2-rearrangement should be more common in the chemistry of azo compounds upon appropriate activation (e.g., protonation, complexation) and substitution of the diazene function.

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(27) (a) Maquestiau, A.; Van Haverbeke, Y.; De Meyer, C.; Duthoit, C.; Meyrant, P.; Flammang, R. *Nouv. J. Chim.* **1979**, *3*, 517. (b) Maquestiau, A.; Van Haverbeke, Y.; Flammang, R.; Meyrant, P. *Org. Mass Spectrom.* **1980**, *15*, 80.

(28) Sauers, R. R.; Beisler, J. A. *J. Org. Chem.* **1964**, *29*, 210.

(29) (a) Sasaki, T.; Eguchi, S.; Toru, T. *J. Org. Chem.* **1976**, *41*, 1803. (b) Sasaki, T.; Eguchi, S.; Toru, T. *J. Org. Chem.* **1971**, *36*, 2454.