J. Am. Chem. Soc. **1993**, *115*, 2217-2220

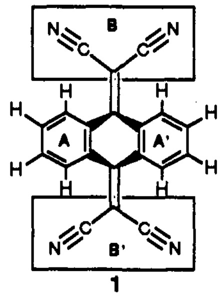
A Structural Steric Isotope Effect in Deuterated Tetracyanoanthraquinodimethane

Norman E. Heimer* and Daniell Lewis Mattern*

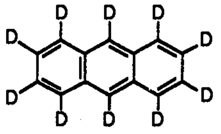
Contribution from the Department of Chemistry, University of Mississippi, University, Mississippi 38677. *Received June 8, 1992. Revised Manuscript Received December 22, 1992*

Abstract: Tetracyanoanthraquinodimethane (TCAQ, **1**) is distorted from planarity into a bent "butterfly" shape due to steric repulsion between its cyano groups and the encroaching peri hydrogens. An X-ray structure determination of perdeuterated TCAQ (TCAQ-d_8, **4**) showed smaller *b* and *c* unit cell dimensions compared to TCAQ. The shortening along the *b* axis (which is roughly perpendicular to the central ring) from 10.022 Å for TCAQ to 9.992 Å for TCAQ-d_8 indicates a combination of closer packing of the TCAQ-d_8 molecules and/or flattening of the butterfly shape. A 0.39° widening in the dihedral angle between the benzene rings in **4**, relative to **1**, is consistent with such a flattening, as is closer approach of the cyano group atoms to the benzene rings. Thus, the smaller effective size of carbon-deuterium bonds results in a steric deuterium isotope effect in the crystal structure of TCAQ.

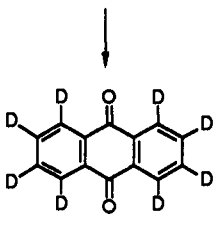
An X-ray crystallographic study[1] has shown that tetracyanoanthraquinodimethane (TCAQ, **1**) is not planar, despite its extended π system. Instead, the central ring is folded: the two benzene rings (A and A′) are raised toward each other like the wings of a butterfly, with a dihedral angle between them of 145°. The dicyanomethylene groups (N≡C—C—C≡N, planes B and B′) are correspondingly bent downward, with a dihedral angle between them of 107°. The presumed cause of this distortion from planarity is an attempt to relieve steric interactions between the four cyano groups and the four peri hydrogens encroaching upon them.[2]



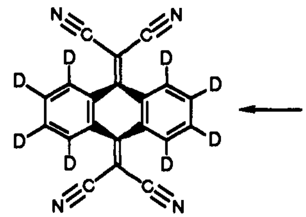
1



2



3



4

We wondered if the substitution of deuteria for protons in the peri positions of TCAQ could give a flatter structure, due to a "steric isotope effect"—that is, due to the smaller effective size of a C–D bond relative to C–H.[3,4] Gas-phase electron diffraction studies of small molecules give an estimate of this effect on bond lengths. For example, the time-averaged C–H bond length in ethene is 1.103 Å, while the C–D bond length in deuterated ethene is 1.099 Å, shorter by 0.004 Å.[5] CD,[6] NMR,[7,8] and IR[8] spectroscopies can detect steric isotope effects on conformational equilibria. Furthermore, many examples are known of rate enhancements when deuterium substitution can relieve steric interactions in congested transition states.[9] The racemization of hindered biphenyls, for example, is faster when ortho hydrogens are replaced by deuteria.[9] The critical steric interaction in this racemization is primarily lateral to the ortho C–H bond rather than end-on; such a lateral interaction is also present in the TCAQ system.

Jaffe and co-workers reported shorter unit cell parameters in the X-ray crystal structure of perdeuterated AIBN compared to perprotio AIBN.[10] As there were no significant differences in intramolecular bond lengths or bond angles, this shortening apparently represents an intermolecular packing effect. To our knowledge, no crystallographic evidence for an *intra*molecular steric isotope effect has been reported. Because of the difficulty of locating hydrogen atoms in X-ray crystallography, the shortening of a C–D bond would have to be "leveraged" through the heavy-atom skeleton to supply such evidence. Pascal and coworkers[11] recently sought such an effect in the highly twisted tetraphenyltriphenylene system. They observed slightly smaller cell parameters for the deuterated isotopomer, which could indicate a more compact, less twisted molecule. However, they judged these differences not to be significant. A steric isotope effect in TCAQ might be observable by a flattening of the butterfly folding in response to shorter C–D, as compared to C–H, peri bonds.

Recent reports[12-14] have described the use of titanium tetrachloride to catalyze the double Knövenagel condensation of quinones with malononitriles. This procedure makes feasible the preparation of perdeuterated TCAQ (TCAQ-d_8, **4**). We report here the X-ray structure of **4** and the evidence for a steric isotope effect in its structure.

Results and Discussion

Anthracene-d_{10} (**2**) was converted by Jones oxidation[15] to anthraquinone-d_8 (**3**); treatment of **3** with malononitrile and $TiCl_4$ gave TCAQ-d_8 (**4**). Single crystals of **4** suitable for X-ray analysis

---

(1) Schubert, U.; Hünig, S.; Aumüller, A. *Liebigs Ann. Chem.* **1985**, 1216.

(2) A Dreiding model of **1** suggests that the central ring has some flexibility: the A–A′ angle can be reduced from 180° to about 167° without appreciable angle strain. However, considerable effort is needed to reduce this angle further to the X-ray structure value of 145°.

(3) Collins, C. J.; Bowman, N. S., Eds. *Isotope Effects in Chemical Reactions*; Van Nostrand Reinhold: New York, 1970; pp 56–63.

(4) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 189–197.

(5) Bartell, L. S.; Roth, E. A.; Hollowell, C. D. *J. Chem. Phys.* **1965**, *42*, 2683–2686.

(6) Barth, G.; Djerassi, C. *Tetrahedron* **1981**, *37*, 4123.

(7) Anet, F. A. L.; Basus, V. J.; Hewett, A. P. W.; Saunders, M. *J. Am. Chem. Soc.* **1980**, *102*, 3945.

(8) Anet, F. A. L.; Kopelevich, M. *J. Chem. Soc.* (*B*) **1970**, 1123.

(9) Carter, R. E.; Melander, L. *Adv. Phys. Org. Chem.* **1973**, *10*, 1–27.

(10) Jaffe, A. B.; Malament, D. S.; Slisz, E. P.; McBride, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 8515.

(11) Pascal, R. A., Jr.; Van Engen, D.; Kahr, B.; McMillan, W. D. *J. Org. Chem.* **1988**, *53*, 1687.

(12) Ong, B. S.; Keoshkerian, B. *J. Org. Chem.* **1984**, *49*, 5002.

(13) Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1984**, 618.

(14) Aravinda, K.; Mays, M.; Cowan, D. *J. Chem. Soc., Chem. Commun.* **1985**, 286.

(15) Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; Longman: London, 1978; pp 786–787.

0002-7863/93/1515-2217$04.00/0

Table I. Unit Cell Parameters for **1** and **4**[a]

crystal	θ range	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)
1 (lit.[b])		9.082(2)	10.013(5)	10.094(5)	109.59(3)	116.60(4)	95.50(4)
1	$5.8 < \theta < 11.8$	9.080(1)	10.022(1)	10.106(1)	109.57(1)	116.45(1)	95.65(1)
	$6.2 < \theta < 14.8$[f]	9.080(1)	10.022(1)	10.106(1)	109.58(1)	116.45(1)	95.64(1)
	$6.0 < \theta < 11.6$	9.082(1)	10.021(1)	10.112(1)	109.58(1)	116.47(1)	95.62(1)
1 av[c,d]		9.081(1)	10.022(1)	10.108(3)	109.58(1)	116.46(1)	95.64(1)
4	$\theta < 12.0$	9.077(2)	9.984(2)	10.093(2)	109.48(2)	116.74(2)	95.44(2)
	$4.4 < \theta < 13.1$	9.077(3)	10.000(1)	10.099(1)	109.47(1)	116.70(2)	95.52(2)
	$5.8 < \theta < 9.8$	9.080(1)	9.991(1)	10.092(1)	109.50(1)	116.71(1)	95.48(1)
	$6.1 < \theta < 13.8$	9.086(4)	9.987(2)	10.093(3)	109.46(2)	116.74(3)	95.45(4)
	$6.2 < \theta < 14.9$[f]	9.080(1)	9.996(1)	10.097(1)	109.52(1)	116.70(1)	95.48(1)
	$6.0 < \theta < 11.6$	9.078(1)	9.994(1)	10.097(1)	109.52(1)	116.67(1)	95.47(1)
4′	$4.5 < \theta < 11.0$	9.076(1)	9.990(1)	10.097(1)	109.54(1)	116.68(1)	95.45(1)
	$6.2 < \theta < 14.9$	9.080(1)	9.996(1)	10.100(1)	109.56(1)	116.66(1)	95.45(1)
4 av[d]		9.079(3)	9.992(5)	10.096(3)	109.51(4)	116.70(3)	95.47(3)
p[e]		0.5	0.0001	0.0003	0.01	0.0001	0.0001

[a] Each entry indicates an independent determination (with esd) of the unit cell parameters. [b] Reference 1. [c] Omitting literature data. [d] Average (SD). [e] Two-tailed p values from t tests comparing means from **1** and **4**. [f] Unit cell used to calculate bond lengths, bond angles, and interplanar angles.

were obtained by crystallization from THF. Crystals of **1** were obtained by a similar route.

Using the atom positions of **1** as the starting point, the structure of **4** was refined to give $R_w = 0.043$ and $R_u = 0.031$. Experimental details and tables of bond length and bond angle are given in the supplementary material. In general, the structure of **4** was quite similar to the published structure[1] for **1**. For non-hydrogen atoms, the average differences between the fractional coordinates reported for **1** and found for **4** were 0.0004 for x/a, −0.0001 for y/b, and 0.0003 for z/c. Bond length comparisons between the two structures showed no significant differences.

However, the unit cells for **1** and **4** seemed to be different. Because the difference was small, multiple determinations of unit cell parameters were carried out over several θ ranges, using two different crystals of **4** and one crystal of **1** (Table I). Crystals on their mounting pins were removed from the goniometer head and replaced in an arbitrary position between measurements, and determinations of unit cell parameters of **1** were made in between those of **4**. To avoid problems that might arise in comparing unit cell data from different diffractometers operating under different conditions, we used only unit cell data from this study in calculating the average unit cell parameters for **1** (Table I). Unit cells used to calculate the bond lengths and interplanar angles of **1** and **4** were obtained from the setting angles for the same list of reflections; the published fractional coordinates[1] were used for **1**.

With several independent determinations of the cell parameters, it was possible to subject the values to the t test for statistically significant differences.[16] All unit cell parameters for **4**, except a, were found to differ significantly from those for **1**. The largest difference was the 0.030 Å shortening of the b cell parameter, from 10.022 Å for **1** to 9.992 Å for **4**.

Shortening of the unit cell in the b direction could, in principle, be the result of either flattening of the molecules along that axis (an intramolecular effect) or closer packing between molecules due to shorter C–D bonds at points where intermolecular contact is made (as observed for AIBN[10]). The molecules of TCAQ lie roughly in the ac plane of the unit cell (see Figure 1a; the dihedral angle between the ac plane and plane E [vide infra] is 37.5°); benzene rings of adjacent molecules overlap in a stacking manner, π cloud to π cloud (Figure 1b). This makes it unlikely that shortening of the Ar–D bond lengths would cause much intermolecular compression along the b axis, since the Ar–D bonds are not directed along b (Figure 1b).[17] However, an intramolecular flattening of the butterfly distortion *would* cause a shortening of the b cell parameter in **4** relative to **1**, consistent with our observations.

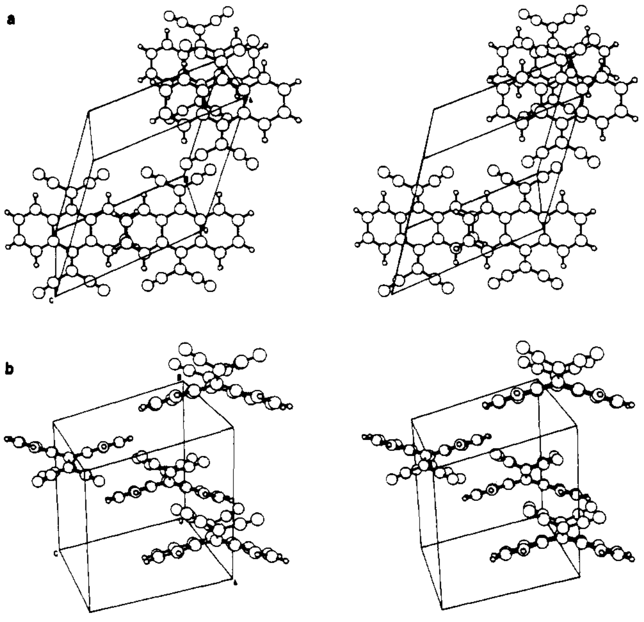


Figure 1. X-ray structure of molecules of **4** within unit cell axes. (a) View roughly normal to planes C, D, and E; (b) view roughly parallel to planes A and A′.

Table II. Dihedral Angles between Planes in TCAQ and Derivatives

	experimental (X-ray)		calculated (AM1)			
planes	**1** (H_8)[a]	**4** (D_8)	**1** (H_8)	**4** (D_8)	**5** (N_4)	**6** (F_4)
A–A′	144.60°	144.99(7)°	137.75°	137.77°	144.96°	128.92°
B–B′	106.66°	106.99(10)°	104.44°	104.43°	120.77°	86.40°

[a] Reference 1.

A comparison of dihedral angles between least-squares planes A and A′ (Table II) revealed flattening in **4** relative to **1** by 0.39°. The corresponding opening in the B–B′ dihedral angle was 0.33°. The widening of these angles can be estimated by trigonometric analysis to result in a 0.026 Å thinner[18] TCAQ molecule along its nominal C_2 axis, that is, roughly in the b direction. There are two molecules in the unit cell along the b direction; thus, the A–A′ and B–B′ angle openings account for about a 0.052 Å shortening of the b parameter. This is somewhat larger than the 0.030(5) Å value found, which may reflect a deviation from strict planarity in the A and B "planes". Along the a and c axes, lengthening of the TCAQ profile due to the larger A–A′ and B–B′ angles is

---

[16] Mack, C. *Essentials of Statistics for Scientists and Technologists*; Plenum: New York, 1975; p 44.

[17] We surveyed 46 close approaches of heavy atoms in neighboring molecules and found the average distance was 0.0087 (SE 0.0010) Å shorter in **4** than in **1**. This suggests that there is, in fact, an intermolecular contribution to the shortening of unit cell parameters in **4**.

[18] By "thinner" we mean closer approach, on average, of the four nitrogens to plane E (vide infra).

Table III. Distances (angstroms) between Cyano Atoms and Planes C, D, and E

cyano atom	distance					
	plane C		plane D		plane E	
	1	**4**	**1**	**4**	**1**	**4**
N1	2.132	2.131	2.550	2.540	2.931	2.921
N2	1.818	1.806	2.209	2.190	2.564	2.547
N3	2.047	2.038	2.382	2.373	2.710	2.695
N4	1.982	1.978	2.347	2.341	2.701	2.687
av	1.995	1.988	2.372	2.361	2.726	2.712
mean diff[a]	0.006		0.011		0.014	
p[b]	0.039		0.015		0.001	
C1	1.639	1.635	2.048	2.033	2.421	2.408
C2	1.485	1.480	1.878	1.864	2.236	2.225
C3	1.590	1.583	1.936	1.930	2.272	2.258
C4	1.552	1.549	1.914	1.911	2.265	2.253
av	1.567	1.562	1.944	1.934	2.298	2.286
mean diff[a]	0.005		0.010		0.012	
p[b]	0.006		0.024		0.0002	

[a] Mean of paired differences for (atom-to-plane distance in **1**) − (corresponding distance in **4**). [b] One-tailed probability of the true mean difference being ≤0, from paired t test.

apparently compensated by shorter C–D bond lengths, making the net changes in a and c relatively small.

We looked at C–C distances across the central ring, that is, between the most distant carbons related by nominal mirror symmetry along the short (B to B′) axis of TCAQ. Flattening that involves the A planes should increase these distances. On the B side, the C–C distance increased from 7.089 to 7.094 Å upon deuteration; on the B′ side, the increase was from 7.072 to 7.075 Å. Similarly, flattening that involves the B planes should increase the distances between nitrogens related by nominal mirror symmetry along the long (A to A′) axis of TCAQ. On the A′ side, the N–N distance increased from 7.438 to 7.446 Å upon deuteration; on the A side, the increase was from 7.675 to 7.688 Å. Although these increases were small, they were all in the appropriate direction for flattening of **4**, and the last difference of 0.013 Å is estimated to be significant at the 95% confidence level.[19] The corresponding cyano carbons were also further apart in **4** than in **1**, by about 0.005 Å.

Finally, we examined the distances of the cyano group atoms from planes C, D, and E, defined by proximal, medial, and distal quartets of approximately mm related benzene ring carbons as shown. If the dicyanomethylene planes (B and B′) are flattened in **4**, the cyano atoms should be closer to planes C, D, and E. Because the molecule has only approximate mm symmetry in the crystal and the atoms defining C, D, and E are not actually coplanar, each cyano group was considered separately. Table III shows the distances of the cyano nitrogens and carbons from each of the planes C, D, and E. The data were subjected to paired one-tailed t tests, which showed that the cyano groups are significantly closer to planes C, D, and E in **4** than in **1**, with confidence levels ranging from 96% to 99.98%.

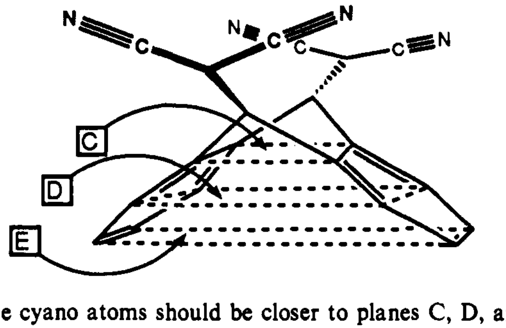
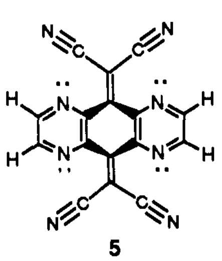
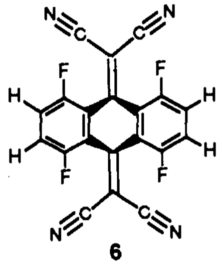


Table III also supports the idea that flattening is occurring in the A plane region. If the flattening were restricted to the B planes, then the cyano atoms in **4** would be closer to each of the planes C, D, and E by the same amount compared to the corresponding distances in **1**. However, upon deuterium substitution, the TCAQ cyano nitrogens approach the C plane least (0.006 Å) and the E plane most (0.014 Å). This requires the E plane to be moving toward the cyano groups to a greater extent than the C plane does—that is, the A–A′ dihedral angle has increased. The closer approach of cyano nitrogens to the distal E plane represents a 0.014 Å flattening of the molecule normal to the E plane, which should be a more reliable indication of shortening along the b unit cell axis than the estimations from dihedral angle openings discussed above. Taking into account the two molecules of TCAQ along the b axis and an angle of 17° between the b axis and the normal to E, the observed flattening corresponds to a 0.027 Å shortening of the b unit cell parameter, in good agreement with the 0.030(5) Å value found.

To provide perspective on these conclusions, we performed AM1 semiempirical molecular orbital calculations[20] on TCAQ and also on TCAQ with the peri C–H bonds shortened by 5% to simulate deuteria (Table II). This is 1 order of magnitude more than the actual effective shortening, as judged by electron diffraction studies.[5] Even so, the shorter C–H bond length did not significantly change the heavy-atom positions in the geometry-optimized structure of TCAQ, which displayed an A–A′ dihedral angle of 137.8° for both **1** and **4**. We also calculated the geometry-optimized structure for a tetraaza-TCAQ (**5**), with nitrogens in place of each peri C–H, and for a tetrafluoro-TCAQ (**6**) (Table II).



5



6

The tetraaza-TCAQ **5** was calculated to be flatter than **1** with a dihedral angle between the benzene ring planes of 145°. This is consistent with an NMR study showing lower side-on steric bulk for a nitrogen lone pair relative to C–H.[21] Finally, the larger steric presence of the fluorines caused more severe folding (to a dihedral angle of 129°) in **6** than in **1**, as expected.

Conclusions. The smaller steric demands of the peri deuteria are reflected in a smaller unit cell, larger A–A′ and B–B′ dihedral angles, and a closer approach of the cyano groups to the benzene rings for TCAQ-d_8 (**4**) than for TCAQ (**1**). Although both intramolecular and intermolecular effects could be involved in principle, the crystallographic data are consistent with an intramolecular flattening of the isotopomer **4** relative to **1**.

Experimental Section

Octadeuterioanthraquinone (3). Decadeuterioanthracene (Aldrich) was oxidized by CrO_3 in aqueous AcOH[15] to form **3**: mp 276–288 °C (lit.[15] mp [for protio **3**] 273 °C); MS, m/e 216 (M^+, 25); 80 (100).

Octadeuterio-11,11,12,12-tetracyanoanthraquinodimethane (4). To a suspension of **3** (1.5 mmol), malononitrile (15 mmol, freshly distilled), and dry pyridine (15 mmol) in 40 mL of dry $CHCl_3$ in a dry flask protected from moisture was added dropwise 7.6 mmol of $TiCl_4$ dissolved in 4 mL of $CHCl_3$. After 5 h of reflux, another charge of $TiCl_4$ was added. After 10 h of further reflux, the mixture was cooled and suction filtered. The resulting solid was triturated under CH_2Cl_2; the filtrate and triturate were combined and washed with H_2O, dried over $MgSO_4$, and concentrated by rotary evaporation. A THF triturate of the resulting solid was flash chromatographed (silica gel, CH_2Cl_2) to give a 12% yield of **4** as a yellow solid. Single crystals were obtained by crystallization from THF or 2-ethoxyethanol: MS, m/e 312 (M^+, 100), 313 (M + 1, 22), 310 (M − D, 17). This pattern repeated, with lower intensities, for M − 28 (loss of DCN) and M − 56 (loss of two DCN). In the mass range

---

(19) Stout, G. H.; Jensen, L. H. *X-Ray Structure Determination*, 2nd ed.; Wiley: New York, 1989; p 404.

(20) The absence of crucial MM2 parameters makes molecular mechanics calculations impracticable for TCAQ.

(21) Imashiro, F.; Takegoshi, K.; Hirayama, K.; Terao, T.; Saika, A. *J. Org. Chem.* **1987**, *52*, 1401.

J. Am. Chem. Soc. 1993, 115, 2220–2226

from 304 to 311, where partially deuterated products would be seen, only the 310 (M − D) peak had intensity >1%.

The **X-ray structure** was determined on an Enraf–Nonius CAD4 diffractometer. The triclinic cell parameters are given in Table I; the structure was refined in space group P$\bar{1}$ (No. 2). Details of the X-ray analysis are given in the supplementary material.

***t* tests** were performed using the InStat program from GraphPAD Software, Inc.

AM1 calculations[22] were performed on a MicroVAX computer using the MOPAC suite of programs.[23]

Acknowledgment. This work was supported in part by the National Science Foundation through Grant No. RII-8902064, the State of Mississippi, and the University of Mississippi.

Supplementary Material Available: Crystallographic data for **4**, including experimental procedures, atomic coordinates, bond lengths, bond angles, torsion angles, and least-squares planes (14 pages). Ordering information is given on any current masthead page.

---

(22) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(23) Stewart, J. J. P. *MOPAC A Semi-Empirical Molecular Orbital Program. QPCE* **1983**, 455.

Theoretical Investigation of the Rotational Barrier in Allyl and 1,1,3,3-Tetramethylallyl Ions

James B. Foresman,[†] Ming Wah Wong,[†,‡] Kenneth B. Wiberg,*[,†] and Michael J. Frisch[§]

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511, and Lorentzian Inc., North Haven, Connecticut 06473.

Received June 29, 1992.
Revised Manuscript Received December 22, 1992

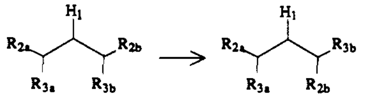
Abstract: Optimized equilibrium geometries and rotational transition structures for allyl and methyl-substituted allyl ions are obtained by using Hartree–Fock (HF) and second-order Møller–Plesset perturbation (MP2) theory. For the parent allyl cation, gas-phase stationary points are also found using the quadratic configuration interaction (QCISD) method. At the levels of theory beyond HF, the lowest energy path for exchange of two hydrogens on one terminal carbon in allyl cation is predicted to involve migration of the central hydrogen to the terminal carbon, whereas the anion transforms via the usual perpendicular transition structure. Allyl cation energies are also computed using the highly accurate CCSD(T) and QCISD(T) methods at the MP2 stationary points. Methyl substitution at the terminal carbon which is involved in the rotation stabilizes the perpendicular structure for the cation, and all levels of theory predict the usual transition structure. Finally, solvation effects on the rotational barrier are investigated using an Onsager reaction field model. The gas-phase rotational barriers of 19.4 and 8.6 kcal/mol calculated for the tetramethylallyl cation and anion, respectively, are reduced to 17.8 and 7.0 in a medium of dielectric constant 78.5.

Introduction

Charge-delocalized carbocations such as allyl cations and nonclassical carbocations have received considerable attention. Allyl cations are of importance because they are involved in a variety of chemical[1] and biochemical processes.[2] Many cations such as the ethyl cation adopt bridged structures, at least in the gas phase.[3] Charge delocalization provides two energetic benefits. First, if electrons flow toward an empty p orbital, a region of low potential energy for an electron, the total energy of the ion will be decreased. Second, in the gas phase, spreading the charge over as large a volume as possible will reduce the electrostatic energy of the ion and make it more stable. Solvents will not affect the first of these terms, but a polar solvent will markedly reduce the importance of the electrostatic energy. As a result, the advantage of bridging will be decreased in the presence of such solvents. Thus, we have begun a series of investigations of the effect of solvents on the properties of charge-delocalized cations.

This report will be concerned with the simplest of these ions, the allyl cation. The barrier to rotation has been used as a measure of the "resonance energy".[4] However, as we have noted, the barrier will arise from both of the terms noted above.[5] A 90° rotation of one methylene group will eliminate the interaction of the π-bond with the cationic p orbital and at the same time will restrict the charge to a smaller volume element, resulting in an increase in the electrostatic energy. We will examine the rotational barrier, the effect of methyl substitution, and the effect of polar solvents. We shall also examine the related allyl anion in order to gain information on the difference between charge-delocalized carbocations and anions. Some difference would be expected since the anions do not have a bonding orbital into which the π-electrons may be delocalized.

There have been many experimental[6] and theoretical[4,5,7] attempts to understand the structure and energetics of rotational isomerism in these ions. There remains some uncertainty regarding the general process:



I I'

[†] Yale University.

[‡] Present address: Department of Chemistry, University of Queensland, St. Lucia, QLD 4072, Australia.

[§] Lorentzian Inc.

(1) For a review, see: Deno, N. C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1970; pp 783–806.

(2) Stryer, L. *Biochemistry*, Freeman: New York, 1988; pp 556–558.

(3) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 384–386.

(4) Mayr, H.; Förner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 6032.

(5) Wiberg, K. B.; Breneman, C. M.; LePage, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 61.

(6) (a) Olah, G. A.; Comisarow, M. B. *J. Am. Chem. Soc.* **1964**, *86*, 5682. (b) Schleyer, P. v. R.; Su, T. M.; Saunders, M.; Rosenfeld, J. C. *J. Am. Chem. Soc.* **1969**, *91*, 5174. (c) Deno, N. C.; Haddon, R. C.; Novak, E. N. *J. Am. Chem. Soc.* **1970**, *92*, 6991.

(7) (a) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649. (b) Cournoyer, M. E.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 5104.

0002-7863/93/1515-2220$04.00/0