Tetrahedron Letters No. 48, pp 4851 - 4854, 1972. Pergamon Press. Printed in Great Britain.

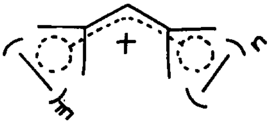
THE STRUCTURE OF A NEW TYPE STABLE CARBONIUM ION BY X-RAY DETERMINATION OF TWO ANALOGOUS SALTS, $[C_{24}H_{18}N]^+BF_4^-$, $[C_{16}H_{12}N]^+ClO_4^-$

Chizuko Kabuto, Masaji Oda, and Yoshio Kitahara*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

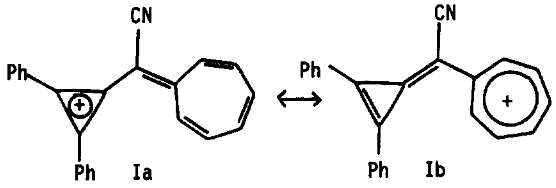
(Received in Japan 13 October 1972; received in UK for publication 24 October 1972)

Recently we have reported the syntheses of some salts of a new type carbonium ion with a positive charge delocalized throughout two rings.[1,2] Since this system should be of a considerable interest to both theoretical and organic chemists, we have determined its detailed structure by X-ray analyses of two salts, $C_{24}H_{18}NBF_4$ and (II), $C_{16}H_{12}NClO_4$. We believe that there are the first structural studies of this system.

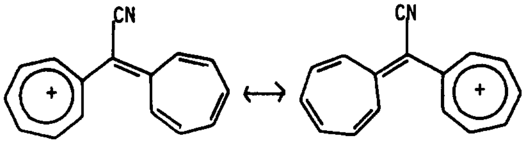


The fluoroborate salt of I, m.p. 228°C and crystallized from acetonitrile-ether belongs to the monoclinic space group $P2_1/c$ with cell dimensions a=7.816, b=16.602, c=15.495 Å, β=104.43°, Dc=1.17 g/cm^3, Z=4. On the other hand, since the fluoroborate salt of II was twinning, the perchlorate salt of II, m.p. 160° and crystallized from methylene chloride-ether was suitable for X-ray analysis and belongs to the monoclinic space group $P2_1/c$, a=9.284, b=11.798, c=14.082 Å, β=111.15°, Dc=1.126 g/cm^3, Z=4. Both salts of I and II were stable in air over the period of data collection. Three dimensional X-ray data were collected using the Rigaku automatically controlled Four Circle Diffractometer with Mo-Kα radiation. Independent reflections within 2θ=55° were applied in the successive calculations. The structures were solved by a symbolic addition method, and refined by the block-diagonal least-squares method with anisotropic thermal motion allowed for non-hydrogen atoms. A difference Fourier synthesis led to the assignment of positional parameters for all hydrogen atoms. The final R-Factors are 0.080 and 0.074 for the salts of I and II, respectively.

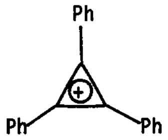
Some details of the molecular geometries are shown in Figures 1 and 2. As a main feature of this system, it should be noted that a pair of cationic rings in molecule have bond alternations to some degree and thus differs from fully conjugated (4n+2)π aromatic system, such as triphenylcyclopropenium cation, III[3] and tropylium cation, IV[4] where all bond lengths in rings are identical. The distribution of the longer and the shorter bonds seem to be



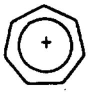
Ia Ib



IIa IIb



III



IV

appear in a triafulvene or a heptafulvene structure. However, the length variation between 1.35 and 1.43 Å reflect only a partial double and single bond character. Thus, it may be concluded that this system is represented as a formal structure, Ia↔Ib or IIa↔IIb where the two resonance hybrids contribute mainly to the ground state.

In molecule, I, a pair cationic rings (three- and seven-membered) have lengths between 1.353-1.403 Å and 1.357-1.420 Å, respectively and thus the bond alternation of the same degree. The shortening of the C(10)-C(8) by 0.036 Å from the C(8)-C(7) bond is a generally accepted value for the corresponding bonds for three membered ring system.[3] Thus, the detailed bond lengths seem to indicate that the two resonance hybrids mentioned above contribute almost equally to each other. This is supported further by its molecular conformation (Figure 1) where the cationic moiety induces planarity while the phenyl ring at the C(11) is twisted to 27.0°.

In contrast, the two seven-membered rings in II, which would be expected to be equivalent, are not cited in any symmetrical situation. This non-equivalence is clearly beyond our experimental error. The exocyclic bonds have a decided difference both in the lengths (1.442 and 1.401 Å) and in the twist angle (36.0 and 13.6°). The more single bond character in the C(7)-C(8) bond than in the C(7')-C(8) may be explained by the greater non-planarity around the bond. Such non-equivalent character among exocyclic bonds seems to cause a small but significant difference in the degree of alternation in the seven-membered ring as compared to the range of the lengths (1.360-1.417 Å in A ring and 1.345-1.433 Å in A' ring). It is interesting to note that these observations suggest a slight inclination toward a 6π cation in A ring and a heptafulvene in A' ring in its character (toward structure IIa). As shown in the twist angles, the entire molecule of II takes a marked non-planar and propeller-like conformation where two rings approximately planar are twisted in the same direction around the exocyclic bonds. In such a conformation, it is unavoidable to make a large angle of 31.6° between planes of rings by a steric force to achieve a limited separation of 2.90 Å for non-bonded C(1)---C(1') distance. This surely results in a great preventation of resonance effect such as IIa↔IIb.

However, H NMR and C^{13} NMR spectral data support equivalent character of the two rings in II, and therefore it is doubtful that the present structure is exclusively adoped in solution. Another plausible model may be a symmetrical propeller conformation with equal twist angle, which would be about 25° by a similar estimation to the case of the triphenylmethylium cation.[5)]

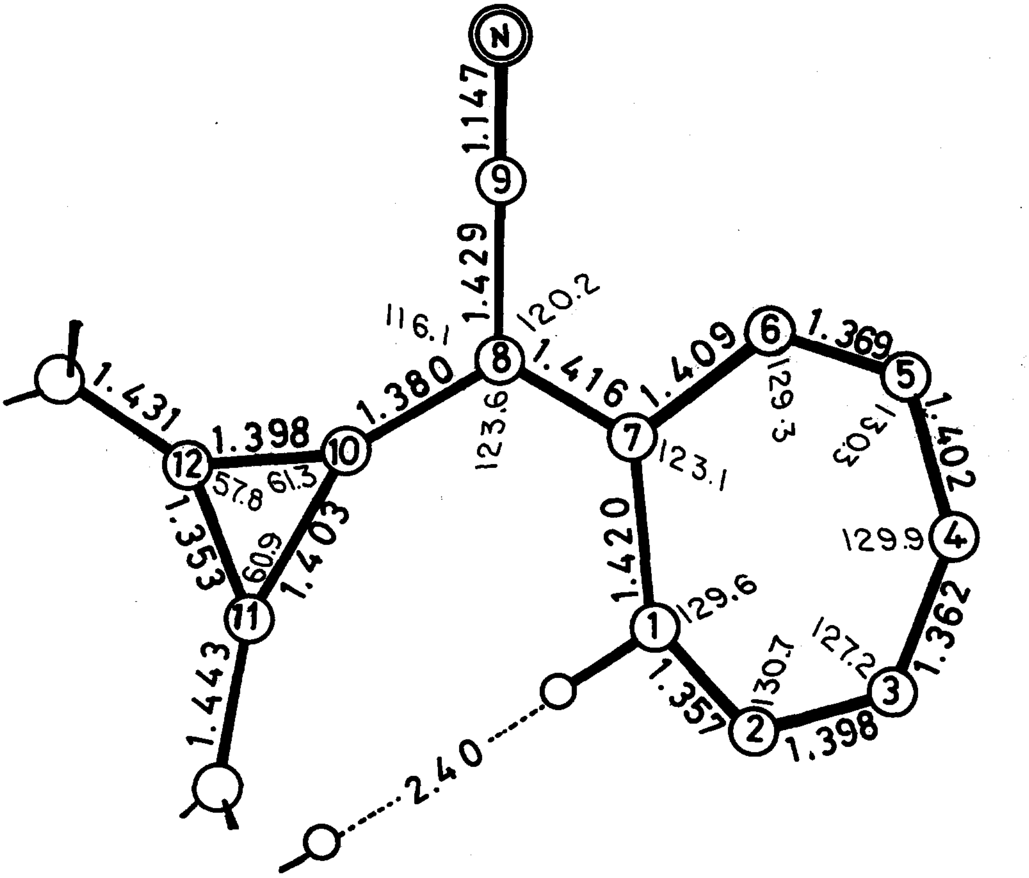


Figure 1. Bond lengths (Å) and angles (°) in the moiety excluding two phenyl groups in the molecule of (I). The estimated standard deviations are av. 0.009 Å and 0.8° for the dimensions in this moiety. The twist angles of exocyclic bonds are C(7)-C(8); 15.2° and C(8)-C(10); 7.6°. The phenyl rings are twisted to 27.0° and 6.5° for one of C(11) and the other of C(12). The dihedral angle between the approximate plane of the seven-membered ring and the plane of the three-membered ring is 10.7°.

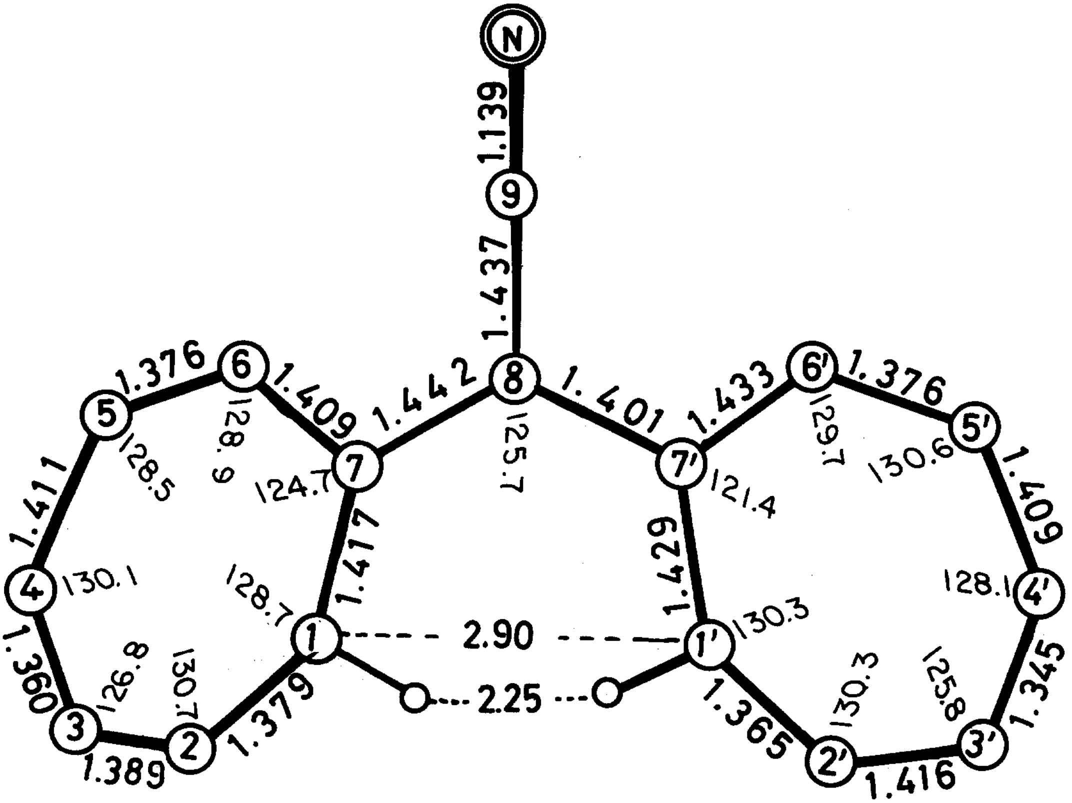


Figure 2. Bond lengths and angles in the molecule of (II). The e.s.d.s' are av. 0.008 Å and 0.7°. The twist angles are C(7)-C(8); 36.0° and C(7')-C(8); 13.6°. The dihedral angle among the approximate planes of the seven-membered rings is 31.5°.

REFERENCES

1) T. Otomo, M. Oda and Y. Kitahara, *Chem. Commun.*, 1971, 114.

2) M. Oda, K. Tamate and Y. Kitahara, *Chem. Commun.*, 1971, 347.

3) M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, 88, 1966, 198.

4) A. I. Kitaigorodskii, Yu. T. Struchkov, T. L. Khotsyanova, M. E. Vol'pin and D. N. Kursanov, *Izuest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1960, 32.

5) J. S. Mckechnie and I. C. Paul, *J. Amer. Chem. Soc.*, 93, 1971, 918.