JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 4, 7–12 (1991)

GEOMETRY OF 2-BENZOPYRYLIUM AND PYRYLIUM CATIONS CALCULATED BY SEMI-EMPIRICAL METHODS. CRYSTAL AND MOLECULAR STRUCTURE OF 1,3-DIMETHYL-6,7-DIMETHOXY-2-BENZOPYRYLIUM PERCHLORATE.

IRINA V. SHCHERBAKOVA,* IOSIF A. YUDILEVICH AND EVGENII V. KUZNETSOV
Research Institute of Physical and Organic Chemistry, Rostov University, 344711 Rostov on Don, U.S.S.R.
DMITRII S. YUFIT AND YURII T. STRUCHKOV
A. N. Nesmeaynov Institute of Organoelement Compounds, USSR Academy of Sciences, Moscow, U.S.S.R.

X-ray data on the crystal and molecular structure of 1,3-dimethyl-6,7-dimethoxy-2-benzopyrylium perchlorate show a good correlation with the geometry of the same cation calculated by the MINDO/3 and MNDO methods with total optimization of all geometrical parameters. The geometry of substituted pyrylium cations was determined by the MNDO and AM1 methods. On the basis of the data obtained, some effects of benzo[*c*]annelation are displayed for the 2-benzopyrylium cation in comparison with the pyrylium cation.

INTRODUCTION

Syntheses and reactions of 2-benzopyrylium salts were described recently in the first review devoted to this class of oxygen cations.[1] The numerous and unusual transformations of this series were discussed in detail in comparison with the monocyclic pyrylium salts [2], i.e. a study of the influence of benzo[*c*]annelation on the pyrylium ring was made on the basis of reactions of 2-benzopyrylium salts. However, the study of the structural characteristic properties of the benzo[*c*]pyrylium cation should be based on the data from physical and theoretical investigations, but until recently this aspect had hardly been studied.[1,3]

The aim of this work was twofold. On the one hand, we used semi-empirical methods of quantum chemical calculations (MINDO/3, MNDO and AM1 with total optimization of all geometrical parameters) for the determination of the geometry of substituted pyrylium and benzo[*c*]pyrylium cations. On the other hand, the crystal and molecular structure of 1,3-dimethyl-6,7-dimethoxy-2-benzopyrylium perchlorate, obtained by x-ray analysis, provided the opportunity of comparing the calculated and experimental data for the same cation. A comparison of the geometries of 2-benzopyrylium and pyrylium cations could also be made and some effects of benzo[*c*]annelation might be revealed on the basis of data obtained for both cations.

RESULTS AND DISCUSSION

As was shown recently,[3] the CNDO/2 method for standard geometry can be successfully applied to the interpretation of the ^{1}H NMR spectra of 2-benzopyrylium salts, whereas some other semi-empirical calculations (MINDO/3 and MNDO) did not give such a satisfactory correlation. However, it is known that the MINDO/3 and MNDO methods with total optimization of all geometrical parameters provide fairly good results in the determination of the geometry of various compounds.[4,5] It should be noted that so far no report on the use of quantum chemical calculations has appeared for structural data on 2-benzopyrylium and pyrylium cations. However, the crystal and molecular structures of a few pyrylium salts with the use of x-ray structural analysis were described,[6–10] but there are no data in the literature on the investigation of 2-benzopyrylium salts by this method.

Taking into account all these facts, we calculated by the MINDO/3[11] and MNDO[12] methods (total optimization of all geometrical parameters) the geometry of 1,3-dimethyl- (**1**), 1,3-dimethyl-6,7-dimethoxy- (**2**), 1-methyl-6,7-dimethoxy- (**3**) and 3-methyl-6,7-dimethoxy-2-benzopyrylium (**4**) cations. Analysis of the

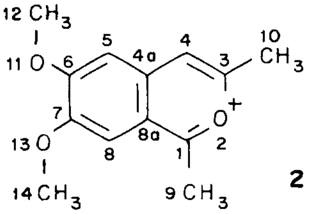
---

* Author for correspondence.

0894-3230/91/010007-06$05.00

Received 24 April 1990
Revised 10 July 1990

Table 1. Calculated bond lengths (Å) and bond angles (°) for the non-hydrogen atoms for **2**



2

Bond	MINDO/3	MNDO	Angle	MINDO/3	MNDO
C(1)—O(2)	1·306	1·337	C(1)—O(2)—C(3)	131·6	123·6
C(1)—C(8a)	1·426	1·420	O(2)—C(1)—C(8a)	115·6	120·0
O(2)—C(3)	1·331	1·360	O(2)—C(3)—C(4)	114·9	119·1
C(3)—C(4)[a]	1·380	1·385	C(3)—C(4)—C(4a)	121·7	121·3
C(4)—C(4a)	1·448	1·438	C(4)—C(3)—C(10)	133·3	127·2
C(4a)—C(5)	1·429	1·417	C(4)—C(4a)—C(8a)	117·5	117·6
C(4a)—C(8a)	1·472	1·450	C(4a)—C(8a)—C(8)	117·5	118·2
C(5)—C(6)[a]	1·406	1·408	C(1)—C(8a)—C(4a)	117·5	118·0
C(6)—C(7)	1·494	1·489	C(4a)—C(5)—C(6)	123·8	121·4
C(7)—C(8)[a]	1·384	1·389	C(5)—C(4a)—C(8a)	117·5	119·5
C(8)—C(8a)	1·464	1·444	C(5)—C(6)—C(7)	118·5	118·7
C(1)—C(9)	1·485	1·518	C(6)—C(7)—C(8)	118·3	119·4
C(3)—C(10)	1·483	1·513	C(7)—C(8)—C(8a)	123·7	121·8
C(6)—O(11)	1·296	1·327	C(8a)—C(1)—C(9)	133·8	127·4
O(11)—C(12)	1·350	1·415	C(5)—C(6)—O(11)	125·3	126·4
C(7)—O(13)	1·316	1·343	C(6)—O(11)—C(12)	137·5	128·8
O(13)—C(14)	1·346	1·410	C(8)—C(7)—O(13)	126·4	126·9
			C(7)—O(13)—C(14)	135·1	128·1

[a] The shortest C—C_{ring} bonds.

data on bond lengths and bond angles for **1–4** revealed more common than different features of the values. Thus, in all cases the C(1)—O(2) and C(3)—O(2) bonds in the fragment of the planar pyrylium ring are shorter than other ring bonds, and therefore the C(1)—O(2)—C(3) ring angle is larger than 120° (Table 1; data on calculations for **1**, **3** and **4** are presented as supplementary material[a]).

It should be noted that substituents do not have much influence on the ring angles and bond lengths in either the pyrylium fragment or the benenzoid annelated ring. The analogous 'neutral' influence of such a substitution has also been described for the charge distribution in various 2-benzopyrylium salts.

Interestingly, the C(3)—C(4), C(5)—C(6) and C(7)—C(8) bonds, marked in Table 1, in all cations **1–4** are shorter than other ring bonds. Hence it is logical to expect a larger contribution for forms **b**, **c** and **e** to the resonance hybrid of the 2-benzopyrylium cation.

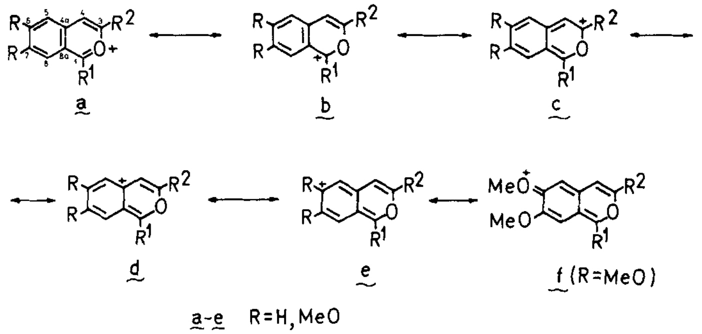
It was obvious that only experimental structural investigations of 2-benzopyrylium salts could give a real estimation of quantum chemical calculations applied to this class of compounds. As was mentioned above, there were no previous experimental data on structural studies of 2-benzopyrylium salts. However, an unusual geometry of the C(1) atom has been assumed for the explanation of ^{13}C NMR spectral data on 1-aryl(methyl)-substituted 2-benzopyrylium salts: an sp^2-hybridized C(1) atom was assumed in the geometry of sp^{3}hybridization [13]. However, crystal growing for x-ray crystallographic work with the aim to proving this assumption was unsuccessful.

In order to verify the data from our calculations, the crystal and molecular structure of 1,3-dimethyl-6,7-dimethoxy-2-benzopyrylium perchlorate (**2**′)[14] was determined by x-ray crystallography. It was found that the crystal of **2**′ contains two independent similar ion pairs **A** and **B** (Fig. 1).

A comparison of the cation geometry by the method described by Razumaeva and Zorkii[15] leads to a low *s*-value (0·03), which corresponds to molecules with equal geometry. Both the cations and the perchlorate anions in the structure **2**′ are located in a special position on the plane, which is passed by all non-hydrogen atoms of the cations and by the Cl, O(4) and

---

[a] Supplementary material is available on request from the authors: atomic coordinates and temperature factors for **2** (x-ray) and calculated bond lengths and angles for **6** (MNDO, AM1) for **1**, **3**, **4** and **7** (MINDO/3, MNDO, AM1).



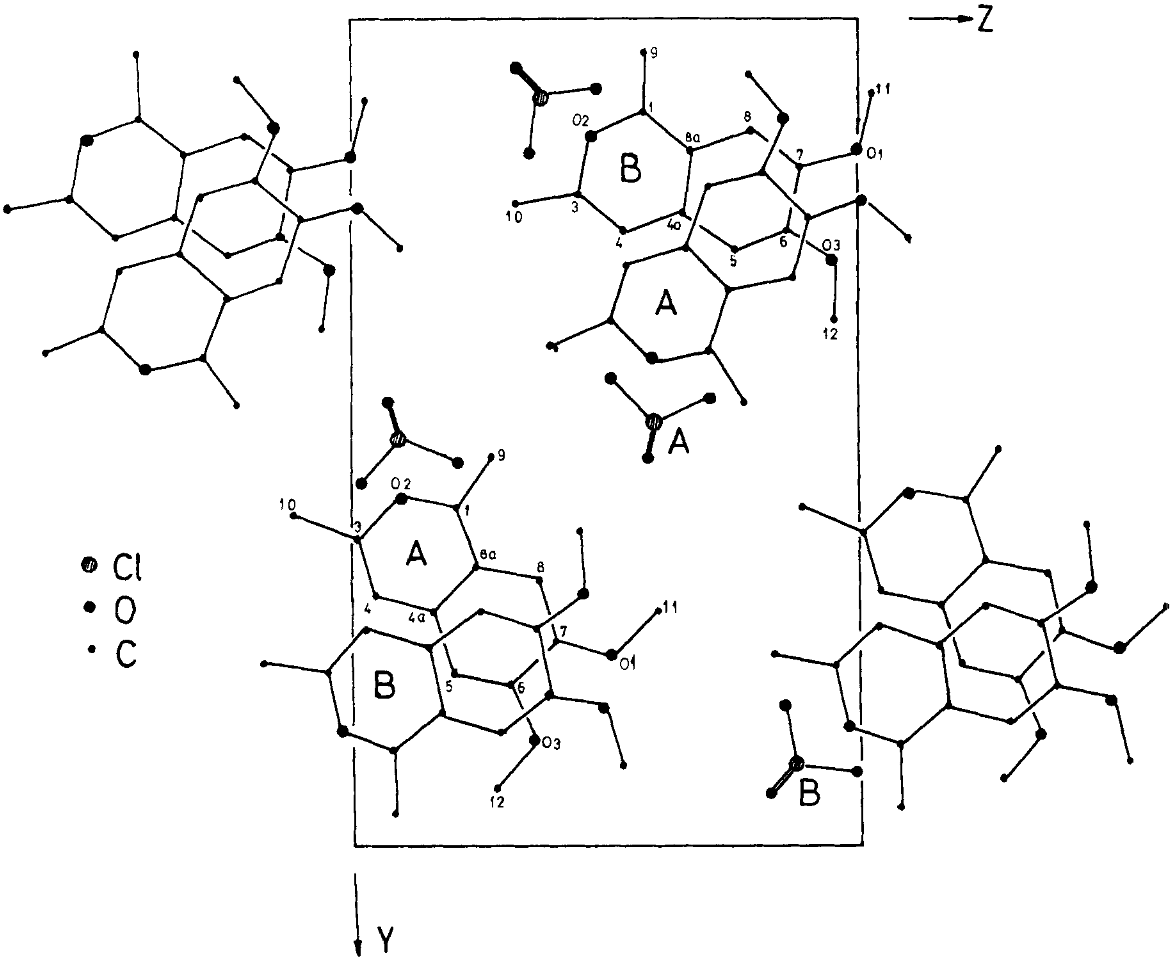


Figure 1. Projection of the structure **2**′ on the DYZ plane (A and B are the two independent ion pairs).

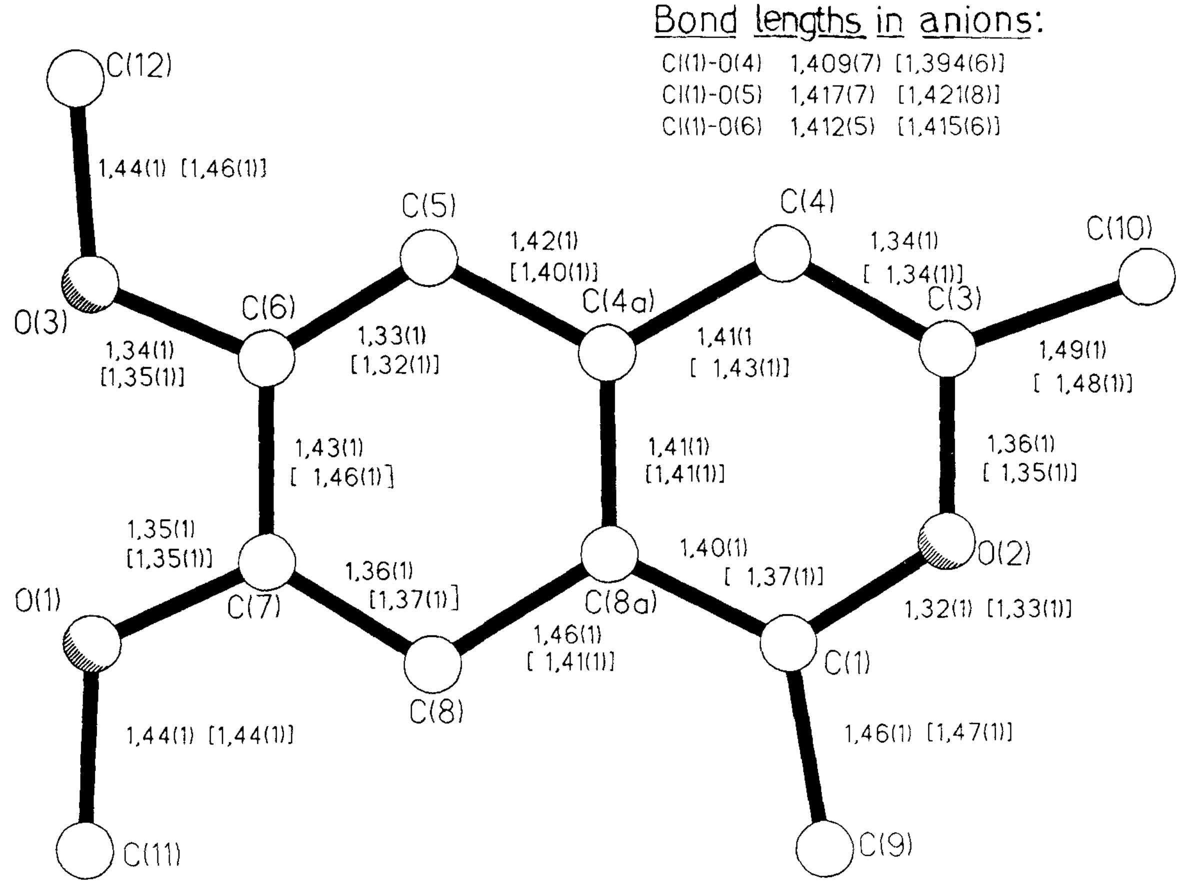


Figure 2. General view of the structure **2**′ with the crystallographic numbering scheme and bond lengths (the values for the second independent pair are given in brackets).

O(5) atoms of the anions. The other O(6) and O(6′) atoms of the anions are linked by this plane. A general view of the cation **2**′ and interatomic lengths (Å) are depicted in Fig. 2. Bond angles are given in Table 2.

Unfortunately, the poor quality of the crystal resulted in a small number of observable reflections, which led to a low accuracy of the geometrical parameters obtained for **2**′. Therefore, a detailed discussion of the specific features of 2-benzopyrylium system could not be made in this case. However, one can note that the C(1)—O and C(3)—O endocyclic bond lengths (Fig. 2) are close to the corresponding experimental values for the monocyclic pyrylium salts (1·33–1·39 Å).[6–8] Evidently, some non-equivalence of these bonds in the 2-benzopyrylium cation **2**′ in comparison with the other ring bonds [the calculated data on **2** gave the same results (Table 1)] is of the same nature as for the pyrylium salts.[2] At the same time, the non-symmetrical position of the oxonium atom towards the methoxy groups in positions 6 and 7 can also influence the C(1)—O and C(3)—O bond lengths in **2**′. The experimental data show normal angle values in the methoxy groups.[16,17]

One can note that the C(3)—C(4), C(5)—C(6) and C(7)—(8) bonds are shorter than other ring bonds (Fig. 2), and in this case the results obtained by the MINDO/3 and MNDO methods for **2**, where the shortest bonds are indicated in Table 1, are in good agreement with the experimental data on **2**′.

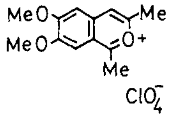
A comparison in the calculated and experimental data on the whole geometry of **2** and **2**′ reveals a small deviation value for MNDO method. It should be noted that the comparison of the experimental and calculated data for standard compounds obtained by Dewar[4] reveals also a better accuracy for the MNDO method. It should be mentioned that the only noticeable difference in the calculated and experimental data on **2** and **2**′ is that the CH_3OC_{ring} bond angles in **2** are markedly

Table 2. Bond angles (°) for the non-hydrogen atoms for **2** (A, B)

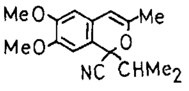
Angle	**2**′(A)	**2**′(B)
O(4)—Cl(1)—O(5)	107·7(3)	107·8(3)
O(4)—Cl(1)—O(6)	111·2(3)	111·5(3)
O(5)—Cl(1)—O(6)	109·3(3)	108·6(3)
O(6)—Cl(1)—O(6)	108·1(3)	108·7(3)
C(7)—O(1)—C(11)	117·2(5)	115·5(5)
C(1)—O(2)—C(3)	123·0(6)	122·7(6)
C(6)—O(3)—C(12)	116·9(5)	117·4(5)
O(2)—C(1)—C(8a)	120·6(6)	120·5(6)
O(2)—C(1)—C(9)	112·8(6)	110·6(6)
C(8a)—C(1)—C(9)	126·6(7)	128·8(7)
O(2)—C(3)—C(4)	120·1(6)	119·5(7)
O(2)—C(3)—C(10)	110·1(6)	111·6(6)
C(4)—C(3)—C(10)	129·8(7)	128·9(7)
C(3)—C(4)—C(4a)	119·9(6)	121·0(7)
C(4)—C(4a)—C(5)	122·0(6)	122·6(6)
C(4)—C(4a)—C(8a)	119·3(6)	117·2(6)
C(5)—C(4a)—C(8a)	118·8(6)	120·2(6)
C(4a)—C(5)—C(6)	119·9(6)	120·3(7)
O(3)—C(6)—C(5)	125·0(6)	126·9(7)
O(3)—C(6)—C(7)	113·1(6)	111·6(6)
C(5)—C(6)—C(7)	121·8(6)	121·5(7)
O(1)—C(7)—C(6)	115·0(6)	114·2(6)
O(1)—C(7)—C(8)	123·0(6)	127·8(6)
C(6)—(7)—C(8)	121·9(6)	118·0(6)
C(7)—C(8)—C(8a)	116·1(6)	121·2(6)
C(1)—C(8a)—C(4a)	117·2(6)	119·1(6)
C(1)—C(8a)—C(8)	121·4(6)	122·2(7)
C(4a)—C(8a)—C(8)	121·4(6)	118·7(6)

arger than those in **2**′ (Tables 1 and 2). Probably in his case the crystal packing factor plays a role.

A comparison of the molecular structures of 1,3-imethyl-6,7-dimethoxy-2-benzopyrylium perchlorate 2′) and 1-cyano-1-isopropyl-6,7-dimethoxy-3-nethylisochromene (**5**)[18] shows that all the C—C ring onds in the benzenoid annelated ring in the latter comound have very close experimental lengths (x-ray tructural analysis), which do not differ from that of he standard aromatic bond.



2′



5

The evident skeletal similarity of **2**′ (**2**) and **5** leads o the obvious conclusion that the described deviations in the benzenoid annelated ring in **2**′ (**2**) are really due to the influence of the pyrylium ring, and, consequently, to the contribution of the resonance forms **b**, **c** and **e**, which are not possible for isochromene **5**.

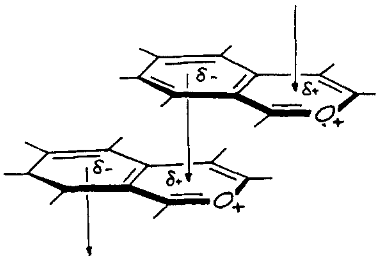
Interestingly, the geometry of 2,6-dimethyl- (**6**) and 2,4,6-trimethylpyrylium (**7**) cations calculated by the MNDO[12] and AM1[19] methods with total optimization of all geometrical parameters shows that the C—C bonds in the pyrylium ring have similar lengths (supplementary material), which are almost identical with the standard aromatic bond length, in contrast to the shorter C(2)—O and C(6)—O bonds. These facts are in good agreement with the experimental data on 2,4,6-triphenylpyrylium salts with different anions,[6–8] where the same characteristics for the geometry of the pyrylium ring have been determined.

It should be noted that the slight effect of the 4-methyl group in the pyrylium ring is too insignificant to be compared with the effect of benzenoid annelation on the C(4)—C(5) bond, which leads to the markedly distinguished geometry of the pyrylium fragment in the newly formed 2-benzopyrylium cation.

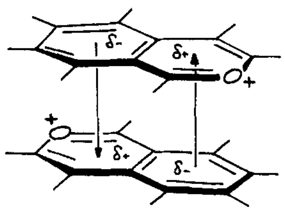
Thus, on the basis of data obtained, one can conclude that the effects of benzenoid annelation on the pyrylium ring and of the heterocyclic fragment on the benzenoid ring are similar to those in the pair pyrydinium–isoquinolinium,[20] but they are more pronounced than in the latter series.

It was proposed recently[1] that the unusual ease of some reactions of 2-benzopyrylium salts is determined by possible stack aggregations of type **C** or **D**, which could be formed analogously to the planar pyridinium salts in solutions,[21] and to the skew *N*-phenyl pyridinium chloride hydrate presenting pairwise aggregates in the crystal.[22]

However, it can be seen in Fig. 1 that in the crystal of **2**′ the cations form the stacks with another orien-



C



D

tation along the *x*-axis with an interplanar distance of 3·41 Å, probably owing to a slight stacking interaction. The shortest distance between atoms of neighbouring cations is 3·48(1) Å for C(7) and C(6′). Thus, at least in the crystal the stack aggregations **C** or **D** are not characteristic for the 2-benzopyrylium cation. Probably the investigation of solutions of 2-benzopyrylium salts could provide some additional information on the possible existence of such remote π-complexes.

CONCLUSION

The geometry of substituted 2-benzopyrylium cations calculated by the MINDO/3 and MNDO methods is mainly in good agreement with the experimental data obtained by x-ray structural analysis. In comparison with data on the calculated geometry of substituted prylium cations by the MNDO and AM1 methods, some effects of benzo[*c*]annelation are displayed for the 2-benzopyrylium cation.

On the basis of the data obtained, one can predict the three most probable centres for nucleophilic attack in the 2-benzopyrylium cation, namely positions 1, 3 and 6, in accordance with the contribution of the resonance forms. However, whereas the nucleophilic reactions at positions 1 and 3 are well-known for 2-benzopyrylium salts,[1] previously no data have been published on such reactions at position 6. The latter pathway is obviously determined not only by the ease of the equilibrium nucleophilic addition to position 6, but also by further intermediate thermodynamic processes which may depend on various structural characteristics of the initial compounds.

EXPERIMENTAL

Crystals of 1,3-dimethyl-6,7-dimethoxy-2-benzopyrylium perchlorate (**2′**)[14] ($C_{13}H_{15}ClO_7$) are rhomboidal (from glacial acetic acid). 0·4 mm × 0·3 mm × 0·2 mm, at −120 °C: $a = 6{\cdot}816(3)$,0 $b = 18{\cdot}554(5)$, $c = 11{\cdot}384(4)$ Å, $V = 1439{\cdot}0(6)$ Å^3, $d_{\mathrm{calc}} = 1{\cdot}43$ mg m^{-3}, space group $Pmn2_1$, $Z = 4$. Unit cell parameters and intensities of 1111 unique reflections from 1111 observed reflections were measured with an automatic four-circle Syntex $P2_1$ diffractometer at −120 °C (Mo Kα radiation, graphite monochromator, $\theta/2\theta$ scanning, $\theta < 30°$). The crystal structure was determined by the direct method and refined by the full-matrix least-squares method in anisotropic approximation for all non-hydrogen atoms. From different series all H atoms were determined and refined with a fixed $B = 5$ Å^2 value. Final $R = 0{\cdot}053$, $R_W = 0{\cdot}040$. All calculations were performed on an Eclipse S/200 computer using INEXTL programs.[23] A list of bond angles is given in Table 2. Bond lengths for **2′** (A, B) and numbering of atoms in Table 2 are given in Fig. 1.

REFERENCES

1. E. V Kuznetsov, I. V. Shcherbakova and A. T. Balaban, *Adv. Hetercycl. Chem.* **50**, (1990) in press.
2. A. T. Balaban, A. Dinculescu, G. N. Dorofeenko, G. W. Fischer, A. V. Koblik, V. V. Mezheritskii and W. Schroth, *Adv. Hetercycl. Chem., Suppl.* **2**, 1 (1982).
3. I. V. Shcherbakova, I. A. Yudilevich and E. V. Kuznetsov, *J. Phys. Org. Chem.* **3**, 575–580 (1990).
4. M. J. S. Dewar, *Further Perspectives in Organic Chemistry*, p. 107. Elsevier, Amsterdam (1978).
5. V. Minkine, B. Simkine and R. Miniaev, *Theorie de la Structure Moleculaire*. Mir, Moscow (1982).
6. T. Tamaura, T. Yamare, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Jpn.* **47**, 832 (1974).
7. N. G. Bokii, R. V. Vedrinskii, V. V. Kitaev, N. A. Lopatina and Yu. T. Struchkov, *Koord. Khim.* **2**, 103 (1976).
8. O. E. Kompan, K. A. Potekhin, N. G. Furmanova and Yu. T. Struchkov, *Zh. Struct. Khim.* **21**, 194 (1982).
9. M. G. B. Drew, G. W. A. Fowles, D. A. Rice and L. J. Shanton, *J. Chem. Soc., Chem. Commun.* 614 (1974).
10. N. Serpone and P. H. Bird, *J. Chem. Soc., Chem. Commun.* 284 (1975).
11. R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. chem. Soc.* **97**, 1285 (1975).
12. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4899 (1977).
13. M. Farkas, W. Voelter and M. Vajda, *Acta Chim. Hung.* **96**, 373 (1978).
14. G. N. Dorofeenko, A. D. Semenov, V. I. Dulenko and S. V. Krivun, *Zh. Org. Khim.* **1**, 1171 (1965).
15. A. E. Razumaeva and P. M. Zorkii, *Zh. Struct. Khim.* **21**, 77 (1982).
16. L. E. Sutton, *Tables of Interatomic Distances and Configuration in Molecules and Ions*, Special Publication No. 18. Chemical Society, London (1965).
17. R. F. J. Bryan, *J. Chem. Soc.* 1311 (1967).
18. I. V. Scherbakova, E. V. Kuznetsov, I. A. Yudilvich, O. E. Kompan, A. T. Balaban, A. H. Abolin, A. V. Polyakov and Yu. T. Struchkov, *Tetrahedron* **22**, 6217 (1988).
19. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.* **107**, 3902 (1985).
20. F. Genet, *Bull. Soc. Fr. Mineral. Crystallogr.* **88**, 463 (1965).
21 Z. Dega-Szafran, M. Szafran and A. R. Katritzky, *J. Chem. Soc., Perkin Trans. 2* 1895 (1985).
22. A. T. Balaban and M. Gheorghiu, *Rev. Roum. Chim.* **23**, 1065 (1978).
23. R. G. Gerr, A. I. Yanovskii and Yu. T. Struchkov, *Kristallografiya* **28**, 1029 (1983).