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THE PROBLEM OF AROMATICITY VERSUS A VINAMIDINIUM STATE IN 2,4-BIS(DIALKYLAMINO)PYRYLIUM SALTS. CRYSTAL AND MOLECULAR STRUCTURE OF 2,4-DI-PYRROLIDINO-6-PHENYL-PYRYLIUM TETRAPHENYLBORATE.

J. C. BARNES[a]*, J. D. PATON[a], R. SPITZNER[b] and W. SCHROTH[b],
a) Chemistry Department, University of Dundee, Dundee DD1 4HN, Scotland,
b). Sektion Chemie, Martin Luther University, Halle 4020, D.D.R.

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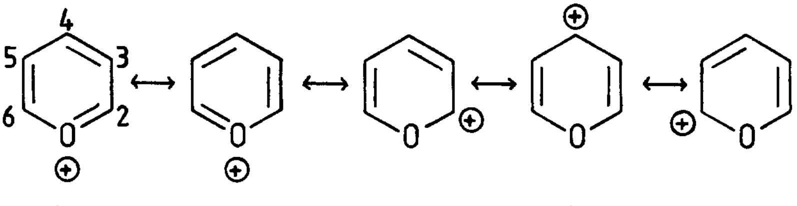
Abstract -- The crystal structure of the title compound confirms the predominance of a trimethine state instead of cyclic aromatic delocalisation in 2,4-dipyrrolidino-6-phenyl-pyrylium salts.

INTRODUCTION

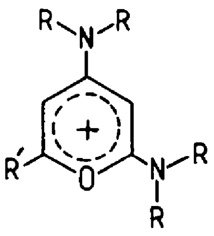
The pyrylium cation I represents the extreme situation of the π-electron perturbation introduced by a single hetero-atom in a benzene ring. The ground state is described by the limiting structures Ia - Ie which show the analogy to an aromatic 6π-electron system (Ia and b ; oxoniabenzene) and, formally, a cyclised pentadienylium cation (Ic - e). Positions 2 and 6 bear the highest electron deficit, evidenced by ^{1}H and ^{13}C-nmr spectra and by theoretical calculations (c.f. review in Ref. 1).



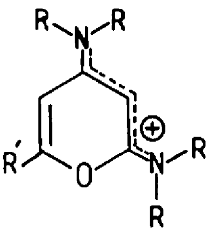
1a 1b 1c 1d 1e

In accordance with an aromatic delocalisation as well as with π-deficient character, most pyrylium salts manifest both a high formation tendency and a high reactivity towards nucleophilic reagents. They undergo ring-opening and ring-transformation reactions of great synthetic importance. However pyrylium salts are not expected to show electrophilic substitution [1].

We have shown recently that 2,4-bis(dialkylamino)pyrylium salts display quite a different behavior. They are uncommonly resistant to nucleophilic attack but readily undergo electrophilic substitutions in the 3-position, a novelty in pyrylium chemistry[2,3,4]. Thus the question arises how far these salts represent a real pyrylium cation with symmetrical π-delocalisation (2a) or a bridged vinamidinium (trimethine) cation (2b). In the latter case two limiting structures 2c and 2d, involving the amino-nitrogen in the π-delocalisation must also be considered.



2a



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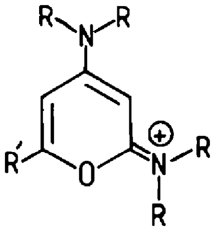

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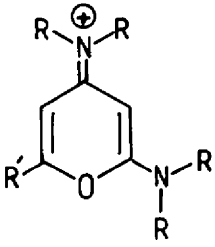
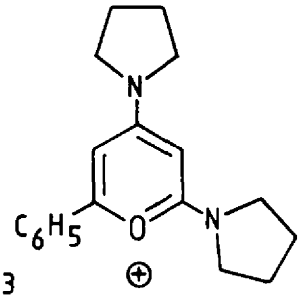


2d

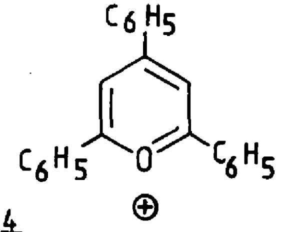
Some conclusions have already been drawn from dynamic nmr-spectroscopy, especially with regard to the restricted rotation about the C-N bonds[5,6,7]. These results are in good agreement with participation of the vinamidinium cation 2b in the ground state. The C-N rotational barrier at $C\gamma$ is higher than that at $C\alpha$ indicating a preference for structure 2d.

The title compound 3 has been prepared recently[2]. The single crystal structure has now been determined for comparison with that of 2,4,6-triphenylpyrylium (4), in the 1,1,3,3-tetracyanopropenide salt[8], in order to clarify the π-bonding in the crystalline material using arguements similar to those of Dähne and Kulpe[9].



3

$^{\ominus}B(C_6H_5)_4$



4

$HC[C(CN)_2]_2^{\ominus}$

EXPERIMENTAL

Crystal data. $C_{43}H_{43}BN_2O$, M_r = 614.65, orthorhombic, $P2_12_12_1$, a = 16.414(5), b = 18.640(6), c = 11.585(6)Å, U = 3544.5 $Å^3$, Z = 4, D_x = 1.15 g cm^{-3}, λ(Cu$K\alpha$ = 1.5418 Å, μ = 4.5 cm^{-1}, F_{000} = 1312, T = 293 K, R = 0.066 for 2113 reflexions.

White laths of the title compound were available from previous studies[2]. After preliminary photographs unit-cell dimensions were refined by precisely centring 12 reflections ($40 \le \theta \le 50^\circ$) on a modified Wooster four-circle diffractometer[10]. Problems with this instrument made it necessary to collect two overlapping partial data sets. Using the diffractometer in the fixed-χ mode with a crystal 0.56 x 0.43 x 0.27 mm mounted along the b-axis, 3383 reflections were measured ($2 \le 2\theta \le 150^\circ$) of which 1539 unique reflexions with $F \ge 7\sigma_F$ were used in the calculations (R_{int} = 0.022). Two crystals of similar dimensions were used for multi-film equi-inclination Weissenberg photographs of layers h (0-16) l and (0,1,5 and 8)kl. The intensities were measured by the S.E.R.C. Microdensitometer Service (Daresbury Laboratory) giving 1516 unique reflexions above background (R_{int} = 0.072).

All calculations were carried out with the *SHELX76*[11], *XANADU*[12] and *PLUTO*[13] program systems on the Dundee University DEC-10 computer. Atomic scattering factors were taken from the library in *SHELX76*.

The structure was solved from the photographic data set after the addition of visual estimates for 40 intense planes at low 2θ which could not be measured by the microdensitometer and 480 unobserved reflections assigned $F = 0.5F_{min}$. The direct methods routine *TANG* showed many of the non-hydrogen atoms and the structure was developed and refined by conventional least-squares refinement and difference syntheses on the observed data only to convergence at R 0.078. Refinement continued after merging the photographic and diffractometer data sets to give 2113 unique reflections ($R_{int} = 0.056$). In the last cycles all non-hydrogen atoms had anisotropic temperature factors, hydrogen atoms were included on calculated positions with isotropic temperature factors refined in groups and the phenyl rings in the anion were included as rigid groups.

Final refinement, minimising $\Sigma w|F_o - |F_c||^2$, 422 refined parameters, $R = 0.066$, $wR = 0.085$, $w = 2.3310/(\sigma_F^2 + 0.000670F^2)$, mean shift/e.s.d. = 0.038, max. shift/e.s.d. = 0.103, max. features on final difference map 0.24, -0.21 eÅ^{-3}.

RESULTS AND DISCUSSION

The crystallographic numbering scheme used [C(13) etc.] is shown in Fig. 1 for the cation and Fig. 2 for the anion. Interatomic distances and angles are given in Table 1. Atomic coordinates and lists of structure factors are available from the authors.

The two pyrrolidine rings are identical and apparently planar, which is chemically implausible. The bonds C(15)-C(16) and C(20)-C(21) are short (1.469(15), 1.382(14)Å) and these atoms appear to have large thermal parameters perpendicular to the ring planes. Probably there is a mixture of wagging of these rings about the central 6-membered ring accompanied by positional disorder of C(15), C(16), C(20) and C(21) to give chemically acceptable puckered conformations for each ring. Attempts to refine a disordered model gave no improvement over the ordered model reported.

The bond angles at N(13) and N(18) sum to 360°, these are trigonal nitrogen atoms with no sign of a lone pair of electrons. The N-C distances to the central ring are practically identical, 1.336(9), 1.338(9)Å. Comparing these values with C-N distances of 1.37Å in *p*-nitroaniline[14] and 1.352Å in pyridine[15] confirms the involvement of the nitrogen atoms in the extended π-system of the cation. Similarly, C(1)-C(7) at 1.491(9)Å is practically identical with the shortened inter-ring bond in biphenyl (1.495Å).

All four rings in the cation are close to co-planar. The angles between normals to the ring planes are 8.2(1)° for the ring at N(13), 3.2(1)° for that at N(18) and 15.6(1)° for the phenyl group, referred in each case to the central ring, each atom of which lies within one standard deviation of the mean plane.

This structure can be compared with the almost symmetrical 2,4,6-triphenylpyrylium ion[8] in which O-Cα = 1.355Å, Cα-Cβ = 1.366Å Cβ-Cγ = 1.404Å and the phenyl groups are 1.463Å from the central ring carbon atoms with the angle O-Cα-Ph = 113.4°. In the present structure C(1)-O(2) and C(3)-O(2) are equal (1.366Å). This distance is not significantly different from the C-O distance in furan (1.371Å)[16]. C(3)-C(4) (1.361()Å) is significantly shorter than C(4)-C(5) (1.405(10)Å). C(5)-C(6) is significantly longer than C(4)-C(5) and C(1)-C(6) could be a full double bond although shorter than C(3)-C(4) by only 2σ. The angles O(2)-C(1)-C(7) (112.3(6)°) and O(2)-C(3)-N(13) (109.4(5)°) are markedly less than 120° and N(18) is tilted towards the phenyl group and away from N(13).

Thus the static and averaged model represented by the crystal structure is somewhat more like the vinamidine 2b than the pyrylium ion 2a in accordance with the n.m.r. results in solution[4]. However in solution form 2d is more significant than 2c whereas in the crystal the N-C bonds are equal and short. It seems clear that the positive charge must lie on the nitrogen atoms rather than the oxygen, but a very detailed analysis of the bond lengths would be premature based on this determination to moderate precision of a system showing relativly high thermal motion and some disorder. Previous attempts at structure determinations of the chloride and bromide salts of this cation were frustrated by severely truncated diffraction patterns, consistent with very high thermal motion and disorder in the crystals. A low temperature structure of the BF_4^- salt might quench the disorder of the pyrrolidine rings and improve the significance of the bond lengths and angles.

The tetraphenylborate anion shows no unusual features (Fig. 2). Cation and anion are far apart and there is no ion-pair interaction in this crystal whereas the 2,4,6-triphenylpyrylium ion was determined in a donor-acceptor complex[8].

Table /.2,4-Di-pyrrolidino-6-phenyl-pyrylium tetraphenylborate.

Interatomic distances (A) and angles(°) .

O2	---C1	1.362(9)	C6	---C1	1.339(10)
C7	---C1	1.491(9)	C3	---O2	1.371(8)
C4	---C3	1.361(10)	N13	---C3	1.338(9)
C5	---C4	1.405(10)	C6	---C5	1.456(9)
N18	---C5	1.336(9)	C8	---C7	1.386(12)
C12	---C7	1.385(12)	C9	---C8	1.405(12)
C10	---C9	1.358(17)	C11	---C10	1.388(17)
C12	---C11	1.432(12)	C14	---N13	1.465(9)
C17	---N13	1.476(10)	C15	---C14	1.520(12)
C16	---C15	1.469(15)	C17	---C16	1.510(13)
C19	---N18	1.480(8)	C22	---N18	1.470(9)
C20	---C19	1.516(12)	C21	---C20	1.382(14)
C22	---C21	1.450(11)	C32	---B31	1.677(9)
C38	---B31	1.694(9)	C44	---B31	1.697(9)
C50	---B31	1.705(9)			

C6	-C1	-O2	121.6(6)	C7	-C1	-O2	112.3(6)
C7	-C1	-C6	126.0(7)	C3	-O2	-C1	119.1(5)
C4	-C3	-O2	123.2(6)	N13	-C3	-O2	109.4(5)
N13	-C3	-C4	127.3(6)	C5	-C4	-C3	118.3(6)
C6	-C5	-C4	117.8(6)	N18	-C5	-C4	123.1(6)
N18	-C5	-C6	119.1(6)	C5	-C6	-C1	119.9(7)
C8	-C7	-C1	120.0(7)	C12	-C7	-C1	118.6(7)
C12	-C7	-C8	121.3(7)	C9	-C8	-C7	117.5(9)
C10	-C9	-C8	120.9(10)	C11	-C10	-C9	123.6(9)
C12	-C11	-C10	115.3(10)	C11	-C12	-C7	121.3(9)
C14	-N13	-C3	126.6(6)	C17	-N13	-C3	121.4(6)
C17	-N13	-C14	111.7(6)	C15	-C14	-N13	104.2(6)
C16	-C15	-C14	107.1(7)	C17	-C16	-C15	106.8(8)
C16	-C17	-N13	104.3(7)	C19	-N18	-C5	122.9(6)
C22	-N18	-C5	126.3(5)	C22	-N18	-C19	110.8(5)
C20	-C19	-N18	103.1(6)	C21	-C20	-C19	109.3(7)
C22	-C21	-C20	112.0(8)	C21	-C22	-N18	104.7(6)
C38	-B31	-C32	114.4(5)	C44	-B31	-C32	112.1(5)
C44	-B31	-C38	102.6(5)	C50	-B31	-C32	104.5(5)
C50	-B31	-C38	112.0(5)	C50	-B31	-C44	111.5(5)
C33	-C32	-B31	119.6(4)	C37	-C32	-B31	120.2(4)
C39	-C38	-B31	121.4(4)	C43	-C38	-B31	118.6(4)
C45	-C44	-B31	120.8(4)	C49	-C44	-B31	119.0(4)
C51	-C50	-B31	117.8(4)	C55	-C50	-B31	122.1(4)

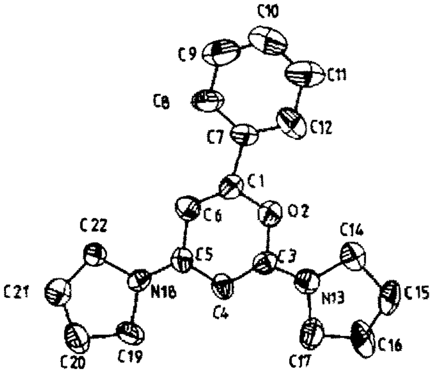


Fig. 1. The 2,4-dipyrrolidino-6-phenylpyrylium cation, showing crystallographic numbering scheme. The extent to which the thermal ellipsoids conceal disorder is discussed in the text.

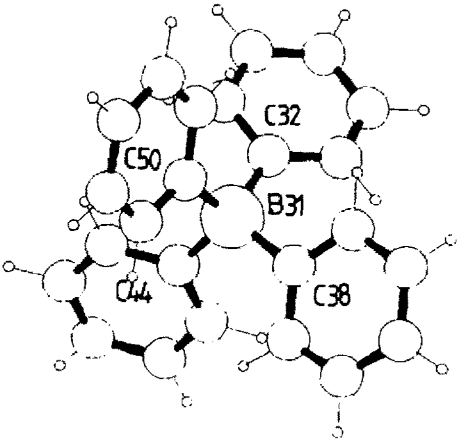


Fig. 2. Tetraphenylborate anion in the title compound.

REFERENCES

[1] A. T. Balaban, A. Dinulescu, G. N. Dorofeenko, G. W. Fischer, A. V. Koblic, V. V. Mezheritskii and W. Schroth, *"Pyrylium Salts: Synthesis, Reactions and Physical Properties"*, Advances in Heterocyclic Chemistry, Suppl. 2 (1982).

[2] W. Schroth and R. Spitzner, *Tetrahedron Lett.*, **26**, 3963 (1985).

[3] R. Spitzner, R. Ragedlia and W. Schroth, *Tetrahedron Lett.*, **26**, 3967 (1985).

[4] W. Schroth, R. Spitzner and E. Kleinpeter, *Tetrahedron Lett.*, **29**, 4695 (1988).

[5] E. Kleinpeter, R. Spitzner and W. Schroth, *Magn. Reson. Chem.*, **25**, 688 (1987).

[6] E. Kleinpeter, R Spitzner, W. Schroth, K. Pihlaja and J. Mattinen, *Magn. Reson. Chem.*, **26**, 707 (1988).

[7] M. T. Chenon, S. Sib and M Simalty, *Org. Magn. Reson.*, **12**, 71 (1979).

[8] T. Tamamura, T. Yamare, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Japan*, **47**, 832 (1974).

[9] S. Dähne and S. Kulpe, *"Structural Principles of Unsaturated Organic Compounds"*, Akademie-Verlag, Berlin, 1977.

[10] J. C. Barnes, W. Golnazarians, J. Iball and J. D. Paton, *Acta Cryst.*, **C39**, 1410 (1983).

[11] G. M. Sheldrick, *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England (1976).

[12] P. Roberts and G. M. Sheldrick, *XANADU*. Program for molecular geometry calculations. Univ. of Cambridge, England (1975).

[13] W. D. S. Motherwell and W. Clegg, *PLUTO*. Program for plotting molecular and crystal structures. University of Cambridge, England (1978).

[14] J. Donahue and K. N. Trueblood, *Acta Cryst.*, **9**, 960 (1956).

[15] B. Bak, L.Hansen-Nygaard and J. Rastrup-Andersen, *J. Mol. Spectr.*, **2**, 361 (1958).

[16] B. Bak, L. Hansen and J. Rastrup-Andersen, *Discus. Faraday Soc.*, **19**, 30 (1955).