

04.1-05 GEOMETRY OF THE $\text{>N}^{\oplus}=\text{C}<$ MOIETY : STRUCTURES OF FIVE RELATED IMINIUM SALTS. By T.G.D. van Schalkwyk, Physics Department, University of the Western Cape, Bellville, 7530 Republic of South Africa.

Crystal and molecular structures of the secondary amine salt bis-(3,5,5-trimethyl-pyrazolinium)hexachlorostanate and five of its condensation products containing an iminium moiety, which up to now has been only rarely described, is fully discussed. Secondary interactions are considered.

ted by the lack of the second component, q_3 .

Table

We are studying the rings through the following expression for the torsion angles ϕ_j .

$$\phi_j \equiv Q \cdot \tau_j = q_2 \cos(S_2 + 2\pi \frac{2j}{7}) + q_3 \cos(S_3 + 2\pi \frac{3j}{7})$$

N	Type	τ_0	τ_1	τ_2	τ_3	τ_4	τ_5	τ_6	S_2	S_3	q_2/q_3
1	B	0	-1	0.4	0.8	-0.8	-0.4	1	90	-	∞
2	TB	-1	0.2	0.9	-0.6	0.6	0.9	0.2	180	-	∞
3	C	0	-1	1.3	-0.9	0.9	-1.3	1	90	90	0.3
4	TC	1	-1.3	1.6	-0.7	-0.7	1.6	-1.3	180	0	0.4
5	TC/TB	-1	0	1.5	-0.9	-0.9	1.5	0	180	0	3.8
6	TC/TB	-1	-1.9	6.2	-3.3	-3.3	6.2	-1.9	180	0	1.3
7	TC/TB	0	-1	2.4	-1.2	-1.2	2.4	1	180	0	1.0
8	BC	0	-1	0.8	0	0	-0.8	1	90	90	1.3
9	S	0	0	-1	2.3	-2.3	1	0	90	270	0.5
10	BS	0	-1	0	1.8	-1.8	0	1	90	270	1.8
11	TS	-1	0.7	-0.2	0	0	-0.2	0.7	180	180	0.4
12	TB/TS	-1	0.7	0	-0.2	-0.2	0	0.7	180	180	0.7
13		0	-1	1.8	-2.3	2.3	-1.8	1	-	90	0
14		1	-0.9	0.6	-0.2	-0.2	0.6	-0.9	-	0	0

B stands for boat, C for chair, S for sofa and T for twist. Q is a proportionality constant.

04.1-06 CONFORMATIONS OF SEVEN-MEMBERED RINGS : A FOURIER TRANSFORM ANALYSIS. By F.H. Cano, C. Foces-Foces and S. García-Blanco, Departamento de Rayos-X, Instituto "Rocasolano", C.S.I.C., Serrano 119, Madrid-6. Spain.

There are several models for dealing with these rings (W.M.J. Flapper & C. Romers, *Tetrahedron* (1975) **31**, 1705; D.F. Bocian et al., *J. Am. Chem. Soc.* (1975) **97**, 687; (1977) **99**, 2876; D. Cremer & J.A. Pople, *J. Am. Chem. Soc.* (1975) **97**, 1354; J.B. Hendrickson, *J. Am. Chem. Soc.* (1967) **89**, 7036 and 7047) but we have found some queries in the description and in the assignment of types when using those models, namely:

- Two different sequences of torsion angles are called boats (W. Henske & R.E. Davis, *Acta Cryst.* (1975) **B31**, 1511; G. Bandoli & D.A. Clemente, *J. Chem. Soc. Perkin II* (1967) 413; P. Chananont et al., *Acta Cryst.* (1980) **B36**, 2115 among other).
- Some types of rings with sequences not having been described, have been spotted (L. Párkányi & G. Argay, *Acta Cryst.* (1976) **B32**, 3316; P.M. Warner et al., *J. Am. Chem. Soc.* (1977) **99**, 5102; H.L. Ammon et al., *J. Am. Chem. Soc.* (1973) **95**, 1968. See table nos. 12 and 13 respectively).

We have studied these discrepancies with the two component description given at the top of the table (F.H. Cano et al., *Acta Cryst.* (1978) **A34**, S91), and we have found some points:

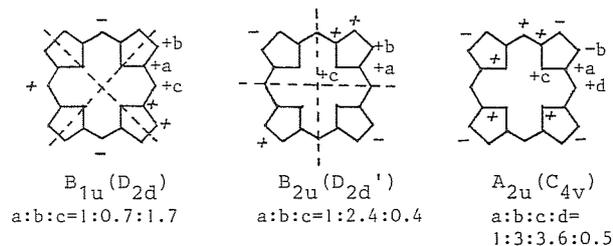
- There is a relationship between our pseudorotation parameters and those of Bocian.
- We think the sequence no. 8 should be called boat-chair (vs. boat-sofa of Flapper et al.) leaving the name boat-sofa for sequence no. 10.
- Sequence no. 12 could be considered a transition between no. 2 (TB) and no. 11 (TS).
- Sequences no. 13 and 14 seem to be different from those of chair or twist-chair (nos. 3 and 4); this is reflected

04.1-07 FLEXIBILITY OF THE PORPHYRIN RING.

By Peter Murray-Rust and Christoph Kratky, Department of Chemistry, University of Stirling, Scotland and Institut für physikalische Chemie, Universität Graz, Austria.

The Cambridge Data File was used to prepare a file of all metalloporphyrins (90 unique molecular fragments). The deviations of atoms from the mean plane through the 24 ring atoms were calculated (GEOM). These were analysed by factor analysis after the 16 possible permutations of labels (in D_{4h}) had been included.

For this 22 dimensional problem, 98% of the observed oop deviation is accounted for by the first 6 factors, which have B_{1u} , B_{2u} , A_{2u} , E_g and B_{2u} symmetry.



All 6 deformation modes leave the pyrrole rings essentially planar, but involve non-planar α -atoms.

The two largest factors (B_{1u} and B_{2u}), which together account for 76% of the observed deformation, correspond very closely to

a harmonic oop deformation of the molecule. A smooth hyperboloid can be fitted to any combination of these ($r=0.997$).

Factor 3 (A_{2u} , 13% of the observed distortion) corresponds to a "doming" of the molecule. It correlates well ($r=0.95$) with the deviation of the metal atom from the least-squares molecular plane.

These 6 factors provide an insight into the way in which metals of varying size distort (or tend to distort) the porphyrin ring. Factors 1 and 2 tend to be induced by "small" ions and factors 3 to 6 by "large" ions.

those between geminal atoms. A potential energy term $V(\phi) = E_{\phi}(1 - \cos^2\phi)$ is included for each of the four torsion angles ϕ about a naphthalene-phenyl link to express the tendency of these moieties to become coplanar. A similar potential $V(\psi) = E_{\psi}(1 - \cos^2\psi)$ for the torsion angles about ring bonds adjacent to these links tends to keep a link in the plane of the ring. Finally, an angle potential $V(\alpha) = (K/2)(\alpha - 120^\circ)^2$ for the two angles α at each ring-link pivot tends to keep them equal.

The potential parameters E_{ϕ} , E_{ψ} , and K are adjusted to make each model have an energy minimum which agrees with the observed crystal structure. Good agreement is obtained with parameters which are similar but not identical for the three compounds.

These calculations were made using computer program WMIN (W. R. Busing, ORNL-5747, Oak Ridge National Laboratory Report, 1981).

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04.1-08 INTRAMOLECULAR POTENTIAL FUNCTIONS FROM OBSERVED CRYSTAL STRUCTURES: 1,8-DIPHENYLNAPHTHALENE, 1,8-DIPHENYLACENAPHTHENE, AND 1,4,5,8-TETRAPHENYLNAPHTHALENE.* William R. Busing, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830 USA

Crystal structures of the title compounds (R.A. Ogilvie, Ph.D. Thesis, Massachusetts Institute of Technology, 1971; R. L. Clough, W. J. Kung, R. E. Marsh, & J. D. Roberts, *J. Org. Chem.* **41**, 3603 (1976); G. Evrard, P. Piret, & M. Van Meerssche, *Acta Cryst.* **B28**, 497 (1972)) show large molecular strains from nonbonded intramolecular interactions and smaller strains from intermolecular packing forces. Assuming that these nonbonded forces can be described by a known potential function, we can deduce the intramolecular torsion and bond angle potentials which are needed to explain the observed structure. This is done by setting up a computational model of the crystal which can be adjusted to a geometry of minimum energy. Potential parameters are selected to make this minimum agree with the experimental crystal structure.

Each molecule is represented by a number of segments: 5, 5, and 9 for the title compounds, respectively. These segments are the naphthalene or acenaphthene moiety, the naphthalene-phenyl links, and the phenyl rings. Each segment is assumed to be rigid with the geometry found in the crystal. The connections between the segments are pivots, each with 2 or 3 rotational degrees of freedom. Additional structural variables are the crystal lattice parameters and the translation and rotation of the molecule as a whole, subject to the constraints of crystal symmetry, for a total of 20, 22, and 17 variables for these compounds, respectively.

The exp-6-1 atom-atom potential of Williams and Starr (*Comp. Chem.* **1**, 173 (1977)) is assumed for all non-bonded inter- and intramolecular interactions except

04.1-09 CLASSIFICATION SCHEME FOR AROMATIC "SOLVATES" IN IONIC ORGANOMETALLIC COMPOUNDS. Jerry L. Atwood, Robin D. Rogers, Duane C. Hrncir, Michael J. Zaworotko, and William E. Hunter, Department of Chemistry, University of Alabama, University, AL 35486.

During the course of our numerous investigations of compounds of the general form $M[AlR_x]$ and $M[Al_2R_6X]$ we have often encountered aromatic molecules of "solvation." Enough structures have now been solved to reveal a distinct pattern of aromatic...cation interaction. This in turn has led to the proposed classification scheme: Class I. Bridging-the aromatic molecule resides between two cations and effects a charge separation; Class II. Terminal-the aromatic is closely associated with (a) one cation, normally in an η^6 -fashion, or with (b) two cations in a sandwich arrangement; Class III. No Cation... Aromatic Interaction. To illustrate this scheme examples will be taken from the literature, but also include the new studies of $[K\cdot DB-18-C-6][AlMe_3NO_3]\cdot 0.5C_6H_6$ (1), $[K\cdot DB-18-C-6][Al_2Me_6O_2]\cdot 1.5C_6H_6$ (2), $[K\cdot DB-18-C-6][Al_2Me_6Cl]\cdot 2.0-C_6H_6$ (3), and $[K\cdot DB-18-C-6][GaMe_3NCS]\cdot 2.5C_6H_6$ (4). Crystal data for the new compounds:

Compound	1	2	3	4
Space Group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a, Å	11.804(4)	13.210(8)	21.319(8)	14.931(7)
b	28.828(6)	13.670(8)	9.512(4)	14.626(7)
c	9.118(3)	14.090(8)	21.081(8)	19.903(8)
α , Deg	-	68.11(4)	-	-
β	96.61(3)	65.46(4)	93.79(4)	107.74(4)
γ	-	87.42(4)	-	-
Reflections	983	1509	2224	2240
R	0.045	0.084	0.050	0.069