

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 |