tinct advantage over the X-ray and neutron diffraction techniques. This is particularly the case for the investigation of materials with characteristic local motion. The sensitivity of the ednmr technique to the determination of the relative positions of light atoms such as protons makes this technique highly complementary to the X-ray crystallographic technique. (It should be noted that the molecular structure, as distinct from the crystal structure, is also partially accessible to nmr studies carried out in nematic solvents.[40])

Ednmr and Hydrogen Bonding. The present studies and investigation of malonic acid by Kwiram and McCalley[18,22] indicate that the empirical equation of Soda and Chiba[41]

$$\frac{e^2Qq}{h} = 310.0 - \frac{571.8}{[R(\mathrm{O}\cdots\mathrm{H})]^3}\ \mathrm{kHz}$$

where $R(\mathrm{O}\cdots\mathrm{H})$ is given in ångström units, should be modified for application to hydrogen-bonded carboxylic acid bridge structures. A more appropriate relationship between the quadrupole coupling constants and the length of the hydrogen bond appears to be

$$\frac{e^2Qq}{h} = 290 - \frac{562}{[R(\mathrm{O}\cdots\mathrm{H})]^3}\ \mathrm{kHz}$$

although we emphasize that further studies are necessary to refine the coefficients.

Comparison of the ednmr data for 1,1-CBDA with that for malonic acid[18,22] indicates that somewhat stronger hydrogen bonding exists in 1,1-CBDA. This difference in hydrogen bond strengths is also reflected in the melting points: 157° (1,1-CBDA) and 135.6° (malonic acid).

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(40) See, for example, the results for cyclobutane reported by S. Meiboom and L. C. Snyder, *J. Chem. Phys.*, **52**, 3857 (1970).

(41) G. Soda and T. Chiba, *ibid.*, **50**, 439 (1969).

Phenalenyl Dimer Cation and Its Electron Paramagnetic Resonance Spectrum[1a]

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Abstract: A new type of dimer cation, formed from a neutral radical and its diamagnetic cation, is reported here. The phenalenyl dimer cation $(C_{13}H_9)_2^+$ is formed on dissolving phenalene in $CF_3COCF_3 \cdot nH_2O$, n = 2–5. Its epr spectrum is described by the coupling constants a_1 (12 H) = 3.108 and a_2 (6 H) = 0.920 G and a g value of 2.002721.

The epr spectrum of the neutral phenalenyl radical was first reported by Calvin, *et al.*,[2] who found it in a CCl_4 solution containing phenalene which had been exposed to air. This radical can be formed in a wide range of organic solvents by dissolving phenalene,[3] which reacts with atmospheric oxygen presumably forming a hydroperoxide, which on decomposition leads to the radical. When the solution is degassed, a well-resolved epr spectrum is obtained. The coupling constants and g value are slightly solvent dependent, but typical values are a_1 = 6.31 G, a_2 = 1.81 G, and g = 2.00260.[3–6]

A different spectrum is obtained when a range of hexafluoroacetone (HFA) hydrates, $CF_3COCF_3 \cdot nH_2O$, n = 2–5, is used as a solvent. This spectrum consists of 13 septets. For n = 4.2 the coupling constants are a_1 (12 H) = 3.108 ± 0.002 G, a_2 (6 H) = 0.920 ± 0.002 G, and the g value is 2.002721 ± 0.000005, the latter having been corrected for second-order effects.[7] No signal was obtained with $n > 6$, and usually one was not obtained if $n \simeq 1.5$, although results were not completely reproducible in this nearly solid hydrate. When dimethoxyethane was present as well as HFA·1.5H_2O only the phenalenyl signal was obtained. When D_2O was used instead of H_2O no deuteration of either phenalenyl or the new radical was detected in their spectra.

In one experiment in HFA·2.5D_2O the spectra of phenalenyl and the new species were superimposed; however, the former species disappeared in a short time. Precise absolute coupling constants and g values were not obtained for this sample but good differential measurements were obtained and will be discussed below.

Since the new spectrum may be derived from that of phenalenyl by doubling the number of each type of proton and halving the coupling constants, it is clearly a dimeric species. Since the spectra are quite sharp, (the dimer line width is 88 mG compared with 80 mG for monomer in the same sample) there can be only one unpaired electron, pointing to a dimeric ion. The chemistry indicates that this must be the dimer cation $(C_{13}H_9)_2^+$. Thus the anion would be unlikely to form

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(1) (a) Issued as NRCC No. 12688. (b) National Research Council of Canada Visiting Scientist 1967–1968.

(2) P. B. Sogo, M. Nakazaki, and M. Calvin, *J. Chem. Phys.*, **26**, 1343 (1957).

(3) A. H. Reddoch, D. H. Paskovich, and A. E. Goggins, to be submitted for publication.

(4) J. E. Bennett, *Proc. Chem. Soc.*, 144 (1961).

(5) B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

(6) A. H. Reddoch, C. L. Dodson, and D. H. Paskovich, *ibid.*, **52**, 2318 (1970).

(7) R. W. Fessenden, *ibid.*, **37**, 747 (1962).

in an acid such as the HFA hydrate.[8] The cation might conceivably be formed directly from the phenalene, since HFA is reported[9,10] to be a hydride ion acceptor. However a more likely route is suggested by the presence of phenalane $C_{13}H_{12}$, found in the reaction mixture by thin layer chromatography. Thus phenalene and the related 1,2,3,5- and 1,2,3,6-tetrahydropyrenes[11] protonate in strong acid and then undergo intermolecular hydride transfer to yield the corresponding phenalenium cations and phenalanes. A similar disproportionation reaction seems to occur in the present system.

The new species is thus analogous to a number of dimer cations which have been studied by optical[12,13] and epr methods including those derived from naphthalene,[14] anthracene,[14] pyrene,[15] perylene,[16] coronene,[17] and mesitylene.[18] The analogy may not be complete, however, for while these dimers have lost one electron from two closed shell molecules, the phenalenyl dimer cation has lost an electron from two open shell molecules. The latter system thus has one electron in the two orbitals derived from the two nonbonding orbitals of its two components, while the other dimers have three electrons in the pair of orbitals based on the highest bonding orbitals of their components. Thus the phenalenyl dimer cation is a new class of dimer cation.

Several dimer cations have been used to test[14] the validity of the Colpa and Bolton relation[19,20] and that of Giacometti, *et al.*[21] (A discussion of these relations has recently been given by Vincow.[22]) However, it is known that proton coupling constants can vary by a few per cent because of vibrational[6] and solvent[3] effects. Since the changes in coupling constants predicted by the above relations are not much greater than these environmental effects, a convincing test would require the elimination of these latter effects. At present this cannot be readily done, particularly for the dimer cations.

The ratio of the coupling constants of the phenalenyl monomer (a_M) and dimer cation (a_D) were measured from the spectrum of the sample containing both species. This procedure does not necessarily avoid the environmental effects. The results are $a_{1M}/a_{1D} = 2(1.027 \pm 0.001)$ and $a_{2M}/a_{2D} = 2(1.001 \pm 0.001)$. This result is not consistent with the relation of Giacometti, *et al.*, which would require the two ratios to be equal. The Colpa–Bolton relation predicts that $a_{2M}/a_{2D} = 2$, since the charge densities at these positions are zero; however, it predicts that $a_{1M}/a_{1D} < 2$, since there is a positive charge at a_{1D} of $e/12$. Thus neither relation is supported by the data but the environmental effects may have a considerable influence.

Similar difficulties may affect the interpretation of g values. From the same spectrum used above $g_D - g_M = (9.1 \pm 0.1) \times 10^{-5}$ (corrected[7] value 9.6×10^{-5}). This may be compared with perylene[16] where $g_D\,(-80°) - g_M\,(25°) = -(9.2 \pm 0.9) \times 10^{-5}$ in CH_2Cl_2 and $g_D\,(-20°) - g_M(25°) = -(1 \pm 2) \times 10^{-5}$ in CH_3CN. For coronene[17] $g_D - g_M = (1 \pm 3) \times 10^{-5}$ using different solvents for monomer and dimer. Clearly discussion is premature.

As with the other dimer cations, the retention of the equivalence of the protons of the monomer components suggests that the dimer cations have a sandwich type structure, although it does not prove it since the spectrum could be merely the time average over a motion through a set of positons of lower symmetry. This structure is quite different from that postulated[23,24] for the dimer which is in equilibrium with the phenalenyl radical. The latter has been regarded as a σ-bonded dimer. The present dimer cation because of its symmetry cannot have such a structure.

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[8] C. G. Krespan and W. J. Middleton, *Fluorine Chem. Rev.*, **1**, 145 (1967).

[9] N. P. Gambaryan and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **4**, 722 (1965).

[10] A. F. Janzen and C. J. Willis, *Inorg. Chem.*, **6**, 1900 (1967).

[11] D. H. Paskovich and N. C. Das, *Chem. Commun.*, 39 (1967).

[12] B. Badger and B. Brocklehurst, *Trans. Faraday Soc.*, **66**, 2939 (1970).

[13] A. Kira, S. Arai, and M. Imamura, *J. Chem. Phys.*, **54**, 4890 (1971).

[14] O. W. Howarth and G. K. Fraenkel, *ibid.*, **52**, 6258 (1971).

[15] J. T. Cooper and W. F. Forbes, *Can. J. Chem.*, **46**, 1158 (1968).

[16] T. C. Chiang and A. H. Reddoch, *J. Chem. Phys.*, **52**, 1371 (1970).

[17] H. van Willigen, E. de Boer, J. T. Cooper, and W. F. Forbes, *ibid.*, **49**, 1190 (1968).

[18] S. Shih and R. M. Dessau, *ibid.*, **55**, 3757 (1971).

[19] J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

[20] J. R. Bolton, *J. Chem. Phys.*, **43**, 309 (1965).

[21] G. Giacometti, P. L. Nordio, and M. V. Pavan, *Theor. Chim. Acta*, **1**, 404 (1963).

[22] G. Vincow, *J. Phys. Chem.*, **75**, 3400 (1971).

[23] D. H. Reid, *Chem. Ind.* (*London*), 1504 (1956).

[24] F. Gerson, E. Heilbronner, A. H. Reddoch, D. H. Paskovich, and N. C. Das, *Helv. Chim. Acta*, **50**, 813 (1967).