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1,3-BIS(1'-ALKYLPYRIDINIUM)CYCLOPENTADIENDIDES: TRIPOLAR MESOMERIC COMPOUNDS?

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The synthesis of the 1,3-bis(diaminocyclopropenylio)cyclopentadienides from the reaction of cyclopentadienides with the 1,2-bis(diisopropylamino)-3-chlorocyclopropenium cation has been reported recently.[2] These compounds, which formally are derivatives of calicene (triapentafulvalene), were described as a new kind of "tripolar mesomeric compound," and represented by structures (I) and (II). Although the 2:1 adducts were the only products isolated, the intermediacy of the appropriate bis(diisopropylamino)calicenes was postulated.

We wish to communicate the preparation of a similar series of compounds derived from the nitrogen analogues of sesquifulvalene (pentaheptafulvalene). These compounds, which consist of a cyclopentadienide or indenide nucleus 1,3-linked to two N-alkylpyridinium rings, are illustrated by the three canonical forms (IIIa-IIIc). Although one of the structures (IIIa) is formally analogous to the tripolar mesomeric form (II), we shall present evidence to indicate that the pyridinium compounds are best represented as hybrids of the cationic forms (IIIb) and (IIIc).

The preparation of a bisymmetrical species is illustrated by the formation of (III). Fulvalenes presumably are intermediates in this reaction, and unsymmetrical isomers (e.g. V, shown in the tripolar form) can be prepared by the reaction of a fulvalene (IV) with an appropriate pyridinum salt. Examples of the synthetic procedures used for the indenides are given below:

(1) Compound (III). 1-Methyl-2-bromopyridinium bromide (4.2 g, 16.6 mmole), indene (0.97 g, 8.3 mmole) and powdered K_2CO_3 (4.0 g, 29 mmole) were stirred together in 50 ml DMF for 24 hr. The solvent was removed *in vacuo*, and the residue extracted with CH_2Cl_2, which was then filtered and evaporated to give 2.2 g of a gummy solid (70%). Recrystallization from MeOH afforded (III) as red needles, m.p. > 230° (dec). An X-ray diffraction analysis of the material is described below.

(2) Compound (V). The addition of 1-benzyl-4-indenylidene-1,4-dihydropyridine[3] (1.13 g, 4 mmole, in 10 ml DMF) to 1-methyl-2-bromopyridinium bromide (0.5 g, 2 mmole) in 10 ml DMF gave an immediate precipitate. After *ca*. 1 hr, the solid was filtered and washed with benzene: yield 0.4 g (30%). Recrystallization from CH_3CN or MeOH gave V as red needles, m.p. 245-246°. Yields can be increased by concentrating the reaction mixture before workup. Anal. Calcd. for $C_{27}H_{23}N_2Br$: C, 71.21; H, 5.09; N, 6.15. Found: C, 70.95;

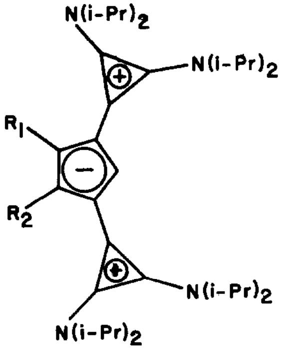
H, 5.04; N, 6.03.

The cyclopentadienides can be prepared in a similar manner from the appropriate starting materials.

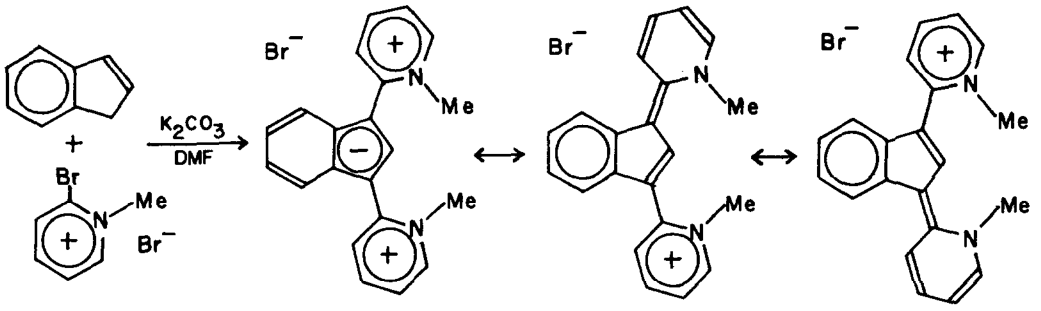
An X-ray diffraction determination of the crystal and molecular structure of (III) has been completed: monoclinic, space group $\underline{P2_1/n}$; $\underline{a}$ = 24.899(2), $\underline{b}$ = 7.681(1), $\underline{c}$ = 9.265(1) Å, $\underline{\beta}$ = 90.92(1)°; $\underline{Z}$ = 4. The intensity data were measured on a Picker FACS-I diffractometer, with Mo$\underline{K\alpha}$ radiation, to a 2$\underline{\theta}$ maximum of 50°: 3115 unique data; 2438 were 3$\underline{\sigma}$ above background. The full-matrix least-squares refinement used anisotropic temperature factors for C, N and Br, and H's were included with isotropic terms. The final $\underline{R}$ index $(\sum|\underline{F}_o - \underline{F}_c|/\sum\underline{F}_o)$ was 0.060.

C-C and C-N bond lengths are given in the Figure. The distances found in the five-ring are quite different from those expected for the indenide portion of a tripolar resonance form.[4] In particular, the C1-C7a and C3-C3a lengths of 1.46 Å are typical of Csp^2-Csp^2 single bonds.[5] Distances in the two pyridinoid rings and in the C2'-C1-C2-C3-C2" region suggest that the compound is best represented as a resonance hybrid of forms (IIIb) and (IIIc). Furthermore, the C2'-C1-C2-C3-C2" distances of 1.40-1.44-1.39-1.44 Å imply that there is more double bond character in the C2'-C1 and C2-C3 bonds than in C1-C2 and C3-C2", which can be interpreted as a larger contribution of the C2'=C1-C2=C3-C2" structure than the C2'-C1=C2-C3=C2" form to the resonance hybrid. This structure, along with the proximity of Br$^-$ to the bottom-most pyridinoid ring in the crystal, suggests that a majority of the + charge is localized in this ring (e.g. IIIb).

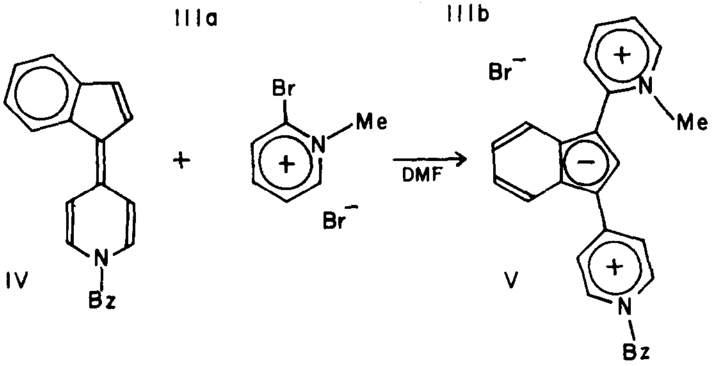
We have found no structural evidence to suggest that (III) is a tripolar mesomeric compound. Rather, the compound is a hybrid of two monopolar, cationic forms (IIIb) and (IIIc), and we believe that further studies of the



I: $R_1 = R_2 = H$
II: $R_1, R_2 = -(CH)_4-$



IIIa IIIb IIIc



IV V

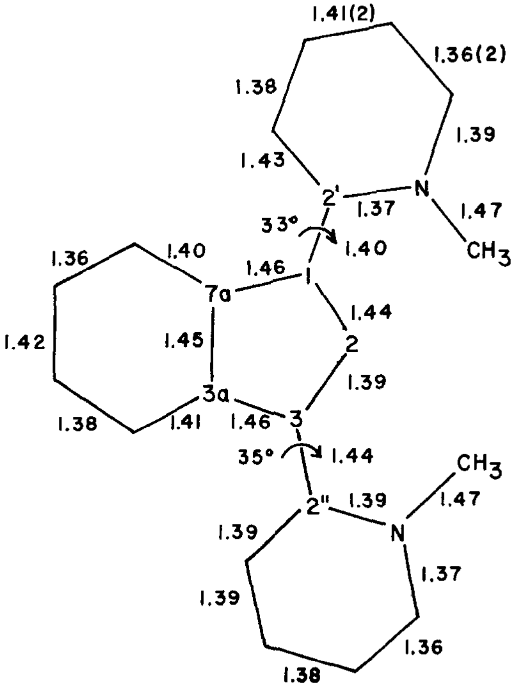


Figure. Bond lengths for 1,3-bis(1'-methylpyridinium)-indenide. The bond length estimated standard deviations are 0.01 Å except where indicated.

cyclopropenium compounds (I) and (II) will show a similar result.

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(3) G. V. Boyd, A. W. Ellis and M. D. Harms, *J. Chem. Soc. C*, 800 (1970).

(4) The five-ring distances in indenyllithium tetramethylenediamine (W. E. Rhine and G. D. Stucky, *J. Amer. Chem. Soc.*, **97**, 737 (1975) are C3a-C7a = 1.429, C7a-C1 = 1.401, C1-C2 = 1.380, C2-C3 = 1.370 and C3-C3a = 1.414 Å.

(5) The central C-C distance in 1,3-butadiene is 1.463 Å (K. Kuchitsu, T. Fukuyama and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1968)).