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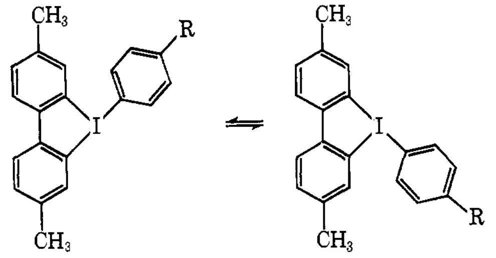
Structure and Stereolability of Triaryliodine(III) Compounds. Degenerate Isomerization of 5-Phenyl-5*H*-dibenziodole

Sir:

We report here the results of nuclear magnetic resonance studies of 5-phenyl- and 5-(*p*-trifluoromethylphenyl)-3,7-dimethyl-5*H*-dibenziodole (**1a** and **1b**) which demonstrate that these triaryliodine compounds have a nonsymmetric planar orientation of iodine–carbon bonds and that the barrier to unimolecular degenerate isomerization is greater than 15 kcal/mol.



1a, R=H
b, R=CF_3

As part of their pioneering studies of high valent organometalloid compounds, Wittig and coworkers[1] reported the synthesis of triphenyliodine by the reaction of diphenyliodonium iodide with phenyllithium. This compound decomposes below −10°, but Clauss[2] subsequently prepared the more stable cyclic analog, 5-phenyl-5*H*-dibenziodole. Studies of the chemistry of these compounds have recently been reported by Beringer and Chang,[3] but little is known of their structure and configurational stability.

Compounds **1a** and **1b** were prepared[2,3a] by the reaction of 3,7-dimethyldibenziodolium iodide[4] with phenyllithium or *p*-trifluoromethylphenyllithium in ether at 0°. The bright yellow solid was twice recrystallized from ether. It is stable at room temperature for several hours and when pure can be stored at −20° for long periods. Solutions are much less stable, but if air and moisture are rigorously excluded they can be kept 1 hr at room temperature with little decomposition.

The nmr spectra of toluene-d_8 solutions of **1a** and **1b** show two singlets in the methyl region (**1a**, δ 1.88, 2.24; **1b**, δ 1.83, 2.21) and a complex aromatic pattern. The observation of nonequivalent methyl signals rules out symmetrical pyramidal or planar structures for **1** and shows that the arrangement of bonds around iodine is similar to that found for $PhICl_2$[5a] which has a planar T-shaped structure,[6] as do other related trisubstituted hypervalent halogen compounds.[5] Solution ^{19}F nmr spectra of BrF_3 give a singlet,[7a,b] but at low temperature[7] and in the gas phase[7c] ClF_3 shows the expected A_2B pattern. An exchange mechanism involving intermolecular fluorine exchange by formation of bridged dimers was suggested for these compounds.

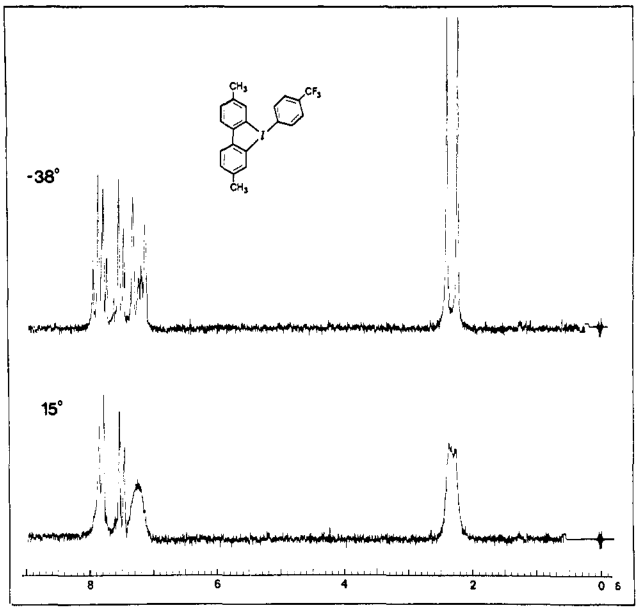


Figure 1. Proton nmr spectra of **1b** in tetrachloroethylene solution at −38 and 15°.

The line shapes of the nmr methyl resonances of **1a** and **1b** show a temperature dependence consistent with a dynamic process which interchanges the environments of the two methyl groups. The coalescence temperatures for solutions in benzene, toluene-d_8, chlorobenzene, tetrachloroethylene, and tetrahydrofuran are between 15 and 60°. Apart from the decomposition, which is quite rapid above 40°,[3a] all line shape changes are reversible.

The low-temperature spectrum of **1b** in tetrachloroethylene (Figure 1, −38°) has methyl singlets at δ 2.24 and 2.41, and an aromatic pattern which can be assigned on the basis of two superimposed 1,2,4-trisubstituted phenyl absorptions. At higher temperatures both the aromatic and methyl peaks broaden (Figure 1, 15°). The simultaneous broadening of the methyl and biphenyl aromatic resonances while the AA′BB′ pattern of the *p*-trifluoromethylphenyl group remains unaffected demonstrates that the temperature dependence is caused by the degenerate isomerization of the aryl substituent between two equivalent sites.

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[1] G. Wittig and M. Rieber, *Justus Liebigs Ann. Chem.*, **562**, 187 (1949); G. Wittig and K. Clauss, *ibid.*, **578**, 136 (1952).

[2] K. Clauss, *Chem. Ber.*, **88**, 268 (1955).

[3] (a) F. M. Beringer and L. L. Chang, *J. Org. Chem.*, **36**, 4055 (1971); (b) F. M. Beringer and L. L. Chang, *ibid.*, 37, 1516 (1972).

[4] W. C. Lothrop, *J. Amer. Chem. Soc.*, **63**, 1187 (1941). The iodonium iodide was purified by crystallization fromdimethyl formamide.

[5] (a) $PhICl_2$: E. M. Archer and T. G. D. van Schalwyk, *Acta Crystallogr.*, **6**, 88 (1953); (b) BrF_3: D. W. J. Magnusson, *J. Chem. Phys.*, **27**, 223 (1957); (c) ClF_3: R. D. Burbank and F. N. Bensey, *ibid.*, **21**, 602 (1953); D. F. Smith, *ibid.*, **21**, 609 (1953). (d) Iodosolactones: W. C. Agosta, *Tetrahedron Lett.*, 2681 (1965).

[6] For a discussion of bonding in hypervalent molecules, see J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969); *J. Amer. Chem. Soc.*, **94**, 1370 (1972).

[7] (a) E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **79**, 322 (1957); (b) E. L. Muetterties and W. D. Phillips, *ibid.*, **81**, 1084 (1959); (c) L. G. Alexakos, and C. D. Cornwell, *J. Chem. Phys.*, **41**, 2098 (1964).

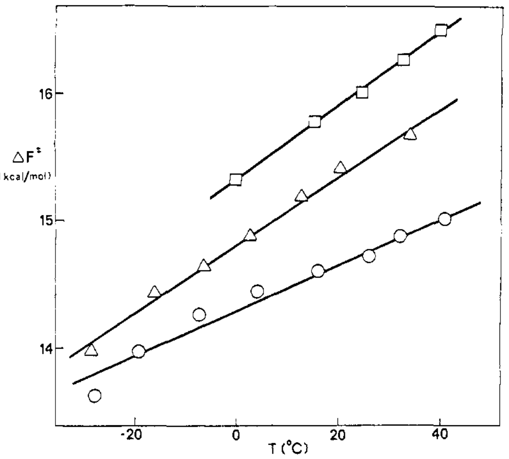


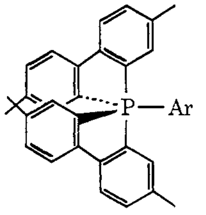
Figure 2. Temperature dependence of free energy of activation: □, **1a** in toluene-d_8; △, **1b** in toluene-d_8; ○, **1b** in tetrachloroethylene. The lines are least-squares fitting of the experimental points and correspond to $\Delta F^{\ddagger}$ (40°) = 16.5, 15.9, and 15.0 kcal/mol, and $\Delta S^{\ddagger} = -29, -27$, and -18 eu, respectively.

Figure 2 presents some results of variable temperature nmr rate studies of **1a** and **1b** by complete line shape fitting using computer generated spectra. To the extent that the large negative entropies of activation are real, these results make it doubtful that the degenerate isomerization is unimolecular.[8] The unreliability of dynamic nmr measurements for determination of activation entropies is well known,[9] and so we have attempted to extend the range of rate measurements to lower temperatures by the Forsen technique of saturation transfer.[10] These attempts were unsuccessful because of inability to cause complete saturation of one methyl peak while observing the other. This is apparently the result of very short spin lattice relaxation times (T_1 from 0.5 to 0.8 sec[11] for **1a**) which require the use of high decoupling power so that interference between observing and decoupling frequencies becomes too large.

Another feature inconsistent with a unimolecular mechanism is the observation that different samples of **1a** or **1b** in the same solvent showed definite variations in isomerization rate. For example, three nmr samples in tetrachloroethylene prepared from the same batch of **1b** showed rate constants of 56, 30, and 69 $\sec^{-1}$ at 15°.[12] Similar results were obtained for toluene-d_8 solutions. We have not, however, been able to trace these rate changes to any experimental variable. Dilution by as much as a factor of four resulted in no detectable change in isomerization rate. Addition of possible complexing agents or catalysts such as tetrahydrofuran, LiF, LiCl, LiBr, LiBr plus Ph_3PO, or benzyltriethylammonium bromide resulted in no change in rate. Addition of tetra-*n*-butylammonium iodide caused a 1.3 rate increase, but this could have been because of introduction of traces of oxygen, which appears to affect the rate slightly.

The available evidence argues against a unimolecular isomerization mechanism, although the barrier for such an isomerization must then be higher than 15 kcal/mol. Bimolecular ligand exchange or bimolecular catalysis can also be ruled out, unless the compound is dimeric in solution or the catalyst concentration does not change upon dilution. The *p*-trifluoromethyl group causes a rate increase, but little significance can be attached to this until more specific mechanistic information is available. In this regard, it would be desirable to have more stable analogs of **1**, and work on this is in progress.

Compounds related to **1**, such as bis(biphenylyl)arylphosphorane (**2**)[13] and bisbiphenylyltellurium (**3**)[14]



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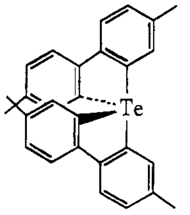

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have been studied by nmr methods. Compound **2** (Ar = β-naphthyl) has $\Delta F^{\ddagger}$ = 11.9 kcal/mol for interchange of methyl environments (pseudorotation).[13a] The compound with Ar = phenyl presumably has an even lower activation energy.[13a] Variable temperature nmr studies of **3** have shown only broadening of the methyl singlet at −55°. No firm conclusions can be drawn from this experiment.[14] The triaryliodine compounds **1** thus appear to exhibit greater configurational stability than related phosphorus compounds (**2**), perhaps a consequence of different hybridization at the central element.[6]

Acknowledgment. We thank Leonard Waldenberger for technical assistance.

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[8] The clearly bimolecular exchange of nonequivalent fluorines in SF_4[7b] has E_a = 4.5 kcal/mol and log A = 7–9. This corresponds to $\Delta S^{\ddagger} = -26$ to -30 eu.

[9] G. Binsch, *Top. Stereochem.*, 3, 97 (1968).

[10] (a) S. Forsen and R. A. Hoffman, *J. Chem. Phys.*, 40, 1189 (1964); (b) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **89**, 760 (1967).

[11] (a) Measurements of T_1 were carried out using the inversion–recovery method, as modified by Freeman and Hill (Varian Associates). R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968); R. Freeman and H. D. W. Hill, *ibid.*, **53**, 4103 (1970).

[12] To account for these rate changes in terms of temperature irreproducibility between samples, that error would have to be 10°, which is highly unlikely. The rate measurements are near coalescence, where the line shape is very sensitive to rate changes. Errors in relative rates are less than ±10%.

[13] (a) D. Hellwinkel, *Chimia*, 22, 488 (1968); (b) G. M. Whitesides and W. M. Bunting, *J. Amer. Chem. Soc.*, **89**, 6801 (1967).

[14] D. Hellwinkel and G. Fahrbach, *Justus Liebigs Ann. Chem.*, 712, 1 (1968).

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Preparation of Stable *closo*- and *nido*-Cobaltaboranes from $Na^+B_5H_8^-$. Complexes of the Formal $B_4H_8^{2-}$ and $B_4H_6^{4-}$ Ligands

Sir:

We report the synthesis, isolation, and structural characterization of several crystalline, air- and water-stable metalloboranes which appear to represent novel metalloboron cage systems. The compounds have been identified as $B_4H_8Co(\pi\text{-}C_5H_5)$ (Ia), 1,2-$B_4H_6Co_2(\pi\text{-}C_5H_5)_2$ (II), 3-c-C_5H_9-1,2-$B_4H_5Co_2(\pi\text{-}C_5H_5)_2$ (III), 4-c-C_5H_9-1,2-$B_4H_5Co_2(\pi\text{-}C_5H_5)_2$ (IV), and 5-$B_9H_{13}Co$-