MeTHF, $\Delta H = -6.3 \pm 0.2$ kcal/mol, $\Delta S = -20 \pm 1$ eu; Na$^+$, THF, -7.4 ± 0.4, -30 ± 2; and Na$^+$, DME, -7.4 ± 0.3, -22 ± 2.[28] These values compare favorably with values for delocalized carbanions determined by proton magnetic resonance[8] and UV.[1b,2]

This great sensitivity of carbon-13 shifts of carbanions to solvent, temperature and cation accounts for the differences in chemical shifts that have been reported for the *same* carbanion.[29] It is especially important to emphasize the danger of comparing chemical shifts of lithium salts to those of the other alkali metals because, even when the shifts are very close, the state of solvation may be significantly different.

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(18) Crystal structure studies for Ph$_3$C$^-$Li$^+$ (ref 19), fluorenyl Li$^+$ and K$^+$ (ref 20, 21), indenyl Li$^+$ (ref 22), and PhCH$_2$$^-Li^+$ (ref 23) show that the cation is close to the α and Cl carbons and is coordinated to the donor site(s) of solvent molecule(s) in the solid state.

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(26) Compared to proton shift changes, a change of 10 ppm in the same solvent is quite large. For example, the *largest* proton shift change observed for trityl carbanions (para hydrogen) was for trityllithium in THF compared to its shift in diethyl ether, 0.37 ppm (ref 8).

(27) For example, for DPM$^-$Li$^+$ in MeTHF, where chemical shift changes are largest, the following chemical shifts are observed at high and low temperatures, respectively: Cl, 146.9, 146.1; C$_m$, 128.7, 127.8; C$_o$, 117.6, 112.5, and 121.4 (average shift = 117.0, ortho carbons are nonequivalent at low temperatures due to slow rotation about the Cα–Cl bond).

(28) Equilibrium constants for the ratio of solvent separated to contact ion pairs were determined using the relationship: $K = \delta_o - \delta_c/\delta_s - \delta_o$, where δ_o, δ_c, and δ_s are the observed, contact, and solvent separated α-carbon chemical shifts, respectively. For DPM$^-$Li$^+$ in MeTHF and for DPM$^-$Na$^+$ in DME, δ_c's were estimated from the linear δ_c vs. 1/M$^+$ plot. For DPM$^-$Na$^+$ in THF, δ_s in DME was used as the solvent separated shift. These estimated values of the experimentally inaccessible δ_c's and δ_s's probably cause the greatest share of the error in the thermodynamic values.

(29) For example, compare the carbon-13 shifts for the lithium and potassium salts of diphenylmethane and triphenylmethane (ref 14–16).

Daniel H. O'Brien,* Charles R. Russell, Alan J. Hart
Department of Chemistry, Texas A&M University
College Station, Texas 77843

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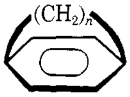
Electron Paramagnetic Resonance of Metastable [7]Paracyclophane: Out-of-Plane Distortions of a Triplet Benzene

Sir:

The recent syntheses of the [7]- and [6]paracyclophanes (I) have made available compounds in which a single benzene ring experiences substantial out-of-plane distortions.[1-3] Unlike the previously prepared [m,m]paracyclophanes (II), the nonplanar π-electron systems are not complicated by inter-ring interactions.[4]



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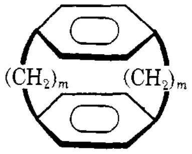

II

III

We have observed the EPR spectrum of the metastable triplet of [7]I (T$_{7\mathrm{I}}$). The average distance between the two unpaired electrons is found to be substantially greater than that observed in triplet benzene or p-dialkylbenzenes. The observations are readily explained by the changes in energy of the π-molecular orbitals as ring carbons 1 and 4 are raised out of the aromatic plane. The degeneracies of the pairs of bonding and antibonding orbitals are split and the two unpaired electrons are largely localized on the out-of-plane carbons. These results also bear on the interpretation of the EPR[5] and optical[6] measurements of [m,m]II.

The EPR spectra of T$_{7\mathrm{I}}$ were determined in methylcyclohexane glasses. The zero-field parameters were[7] $D = 0.1108$ cm^{-1} and $E = 0.0122$ cm^{-1}. In the range of 5-20 K no significant changes with temperature were detected. For [2,2]II, $D = 0.1037$ cm^{-1} and $E = 0.0155$ cm^{-1}. With [3,3]II two isomers were observed; $D = 0.0916$ cm^{-1}, $E = 0.019$ cm^{-1} and $D = 0.077$ cm^{-1}, $E = 0.009$ cm^{-1}. For the relatively strainless [4,4]- and [6,6]II and for p-xylene we were only able to determine $D^* = (D^2 + 3E^2)^{1/2}$. For each of the three $D^* \simeq 0.169$ cm^{-1}. The measurements of de Groot et al. of metastable benzene in a single crystal gave $D = 0.1590$ cm^{-1}, $E = 0.0064$ cm^{-1}; $D^* = 0.1594$ cm^{-1}.[8]

The zero-field parameters D and E are dependent on the distribution of the unpaired spins: $D \propto \langle 3z^2 - r^2/r^5 \rangle$ and $E \propto \langle y^2 - x^2/r^5 \rangle$ where r is the distance between unpaired electrons and x, y, and z are the projections along a set of axes fixed in the molecule. In our systems z will be perpendicular to the plane of the four central carbons, 2, 3, 5, and 6, and y along the C$_1$–C$_4$ direction. D crudely provides an inverse distance between the spins and E a measure of the deviation from threefold or higher symmetry. The nonzero E found for benzene indicates that the average structure is not a regular hexagon.[8]

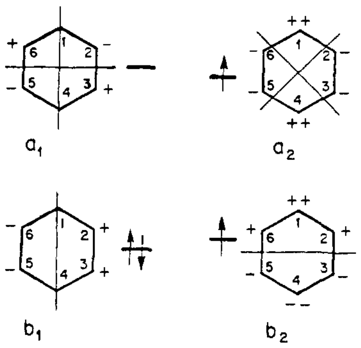

Figure 1. Energies and pictorial representations of the two highest energy bonding orbitals and two lowest energy antibonding orbitals for benzene. The orbital picture corresponds to the planar case but should approximate those for bent structures. The energies refer to the bent structures.

D and D^* for T_{7I} are substantially less than those for p-xylene, [4,4]- or [6,6]II or benzene, assuming any reasonable value for E, e.g., <0.02 cm^{-1}. These D's of ~ 0.16 cm^{-1} are compatible with approximately equal spin distributions around the aromatic ring. The lower value for T_{7I} indicates significantly greater separation between the unpaired electrons as might be expected from resonance structure III. We discuss the preference for this spin distribution in molecular orbital terms.

In planar, hexagonal benzene the highest bonding orbitals, b_1 and b_2, and the lowest antibonding orbitals, a_1 and a_2, form two degenerate pairs. In the lowest triplet state each of these orbitals is equally occupied with an average orbital spin density of $1/2$. The spin is evenly distributed about the ring and $D \approx 0.16$ cm^{-1}.[8]

On bending, carbons 1 and 4 rise out of the plane of the other four. Orbitals b_1 and a_1 have a node passing through C_1 and C_4 (Figure 1). In a simple molecular orbital picture the energy of the levels is determined by the overlap between adjacent atomic orbitals. If a node passes through an atom, the nuclear position does not influence the bonding or antibonding character of the molecular orbital. Consequently, there is no change in the energies of b_1 or a_1 on bending the ring.

The antinodes of b_2 and a_2 occur at C_1 nd C_4. Bending reduces the overlap of C_1 with C_2 and C_6 and of C_4 with C_3 and C_5. The bonding character of b_2 is reduced and the energy of that bonding orbital is raised. Similarly, the antibonding character of a_2 is reduced and its energy lowered (Figure 1).

The configuration of the lowest triplet state of bent benzene is $(b_1)^2$ (b_2) (a_2). The orbitals with the unpaired electrons are largely concentrated at C_1 and C_4. The smaller densities at the other carbons may be viewed as arising from III by allylic resonance. The average distance between the spins increases and D is lower than for the planar hexagonal form. For a more quantitative estimate the distribution of spin density in space must be considered.

The geometry of T_{7I} is unknown. The compensating energy changes for b_2 and a_2 on bending implies substantially easier out-of-plane distortions with T_{7I} than the ground state, S_{7I}, in which the end carbons are already $\sim 17°$ out-of-plane.[9] In addition, the radical character C_1 and C_4 should facilitate nonplanar arrangements of bonds at those atoms. Only small energies are required to bend carbon radicals out-of-plane as is indicated by the stability of bridgehead radicals.[10] The upward and inward motion of C_1 and C_4 on going from the planar to the bent form moves spin density closer to the other ring atoms. The nonplanar arrangements of the bonds to C_1 and C_4 and the rehybridization of the $2p\pi$-orbitals takes spin from the inside to the outside of the boat, away from the remaining π-spin density. With more quantitative information not available we assume that these changes cancel and the spin distribution may be taken as that of a planar, hexagonal ring. The effect of the $-(CH_2)_7-$ chain is then to remove the degeneracies and select the (b_2) (a_2) configuration.

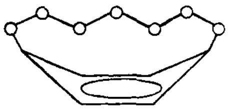

Figure 2. Structure of the ground state of [7]paracyclophane following ref 9.

One can calculate D and E for the bent configuration as 0.1069, 0.0181;[11a] 0.0986, 0.0152;[11b] or 0.0990, 0.0177 cm^{-1},[12] in reasonable agreement with the observed values. This agreement is, in part, fortuitous. The values computed for benzene are very sensitive to the approximations made.[13] However, the calculations referred to here[11,12] satisfactorily reproduce the zero-field splitting for planar benzene. Thus the change on bending from p-xylene to [7]paracyclophane is quantitatively rationalized.

The interpretation of the zero-field parameters for [4,4]- and [6,6]II is straight-forward. The near identity with the result for p-xylene implies that the triplet energy is localized on one aromatic ring on the EPR time scale, $\sim 10^{-10}$ s. Energy hopping is slow.

The optical and EPR spectra of T_{22II} have been interpreted in terms of charge transfer between the aromatic rings in the excited state.[5,6] However, the similarity of D and E for [7]-I and [2,2]-II suggests that out-of-plane bending is more important with the latter. In S_{22II} the end carbons of each ring are bent $\sim 13°$ out of the plane of the central four.[4,14] If the distortion in T_{22II} is sufficient to "freeze" the orbital occupancy of a single ring at (b_2) (a_2) then we expect T_{7I} and T_{22II} to have similar zero-field parameters. Hopping of the excitation between the two rings in [2,2]II (excitonic interaction) will not change the parameters as the rings have parallel orientations for the principal axes.[14,15]

The red shift of the phosphorescence spectrum of T_{22II} in comparison to that of [4,4]II[6] is also likely to have a contribution from the out-of-plane bending. The b_2–a_2 gap is less than it would be in a planar aromatic.

The two isomers for T_{33II} have low values of the zero-field parameters. Rapid energy hopping between nonparallel rings is likely to be involved. Complete or partial freezing of the (b_2) (a_2) configuration by small out-of-plane distortions is also a possible factor.

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(16) Address correspondence to this author at the Chemical Research Center, Allied Chemical, Morristown, N.J. 07964.

E. Wasserman,*[16] R. S. Hutton
Bell Laboratories
Murray Hill, New Jersey 07974

F. B. Bramwell
Brooklyn College
Brooklyn, New York 11210

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The Preparation and Structure of the Linear Tripalladium Cations $(CH_3NC)_8Pd_3^{2+}$ and $(CH_3NC)_6\{(C_5H_5)_3P\}_2Pd_3^{2+}$

Sir:

Reactions between metal ions in different formal oxidation states can be used to form metal-metal bonds. Two examples using reaction partners with d^8 and d^6 electronic configurations are shown in reactions 1[1] and 2.[2]

$$Rh(CNC_6H_{11})_4^+ + RhI_2(CNC_6H_{11})_4^+ \rightleftarrows Rh_2I_2(CNC_6H_{11})_8^{2+} \quad (1)$$

$$17Pt(CN)_4^{2-} + 3PtCl_2(CN)_4^{2-} + 40K^+ + 60H_2O \rightarrow 2K_{20}Pt_{10}(CN)_{40}Cl_3 \cdot 30H_2O \quad (2)$$

In the first case a dimeric, formally Rh(II) species, is formed while in the latter case the solid, known as Krogmann's salt, has a more complex but still well-defined stoichiometry and contains parallel, linear columns of platinum atoms which ideally extend for the full length of a crystal. Equations 3-5

$$(t\text{-}C_4H_9NC)_2PdI_2 + (t\text{-}C_4H_9NC)_2Pd \rightarrow (t\text{-}C_4H_9NC)_4Pd_2I_2 \quad (3)$$

$$(CH_3NC)_4Pd^{2+} + (CH_3NC)_xPd \rightarrow (CH_3NC)_6Pd_2^{2+} \quad (4)$$

$$(CH_3NC)_4Pt^{2+} + (CH_3NC)_xPd \rightarrow (CH_3NC)_6PdPt^{2+} \quad (5)$$

give examples of reactions between complexes with d^8 and d^{10} electronic configurations that also produce metal-metal bonds.[3-5] We now report a new aspect of this chemistry which has led to the preparation and structure of a linear tripalladium complex.

In contrast to reactions 1 and 2 where a single, unique product forms regardless of the reactant stoichiometry, variation of the reaction stoichiometry in the case of reaction 4 alters the product. Addition of 2 mol of $(CH_3NC)_xPd$[6] to $(CH_3NC)_4Pd^{2+}$ or addition of 1 mol of $(CH_3NC)_xPd$ to $(CH_3NC)_6Pd_2^{2+}$ in acetone solution produces $(CH_3NC)_8Pd_3^{2+}$, **1** which has been isolated as the crystalline hexafluorophosphate salt. The infrared spectrum of this solid indicates that only terminal isocyanide ligands are present (ν_{CN} 2221, 2213, 2202 cm^{-1}). The ^{1}H NMR spectrum of this ion in acetonitrile-d_3 consists of a single resonance at τ 6.59.[7] Addition of triphenylphosphine to **1** produces the disubstitution product $[(CH_3NC)_6\{(C_6H_5)_3P\}_2Pd_3](PF_6)_2$, **2**. Like **1, 2** contains only terminal isocyanide ligands (ν_{CN} 2216, 2186 cm^{-1}). Its ^{1}H NMR spectrum consists of a single methyl resonance at τ 6.77 and a phenyl resonance at 2.45, with a 3:5 intensity ratio.[7]

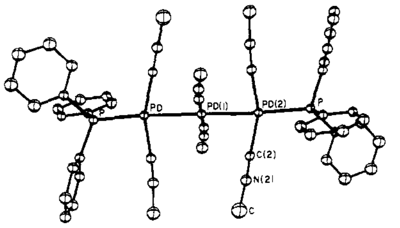

Figure 1. An ORTEP drawing of $(CH_3NC)_6\{(C_6H_5)_3P\}_2Pd_3^{2+}$ showing the 50% thermal ellipsoids.

In order to obtain an accurate and detailed description of the structure of this unprecedented species, an x-ray structural investigation was undertaken. We choose to work with **2** because of its greater stability. Air-stable, red-yellow dichroic crystals of **2** were obtained by slow diffusion in a nitrogen atmosphere of diethyl ether into an acetone solution of the complex containing excess methyl isocyanide and triphenylphosphine. Crystal data (85 K): space group $P\bar{1}$; reduced cell $a = 12.094\ (2)$, $b = 12.127\ (2)$, $c = 10.660\ (2)$ Å; $\alpha = 102.70\ (2)$, $\beta = 112.92\ (2)$, $\gamma = 75.49\ (2)°$; $V = 1380.9$ Å^3; $\rho_{\mathrm{exptl}}{}^{298} = 1.60$, $\rho_{\mathrm{calcd}}{}^{85\,\mathrm{K}} = 1.66$ g/cm^3 for $Z = 1$; $\mu_{\mathrm{MoK}\alpha} = 11.7$ cm^{-1}. Intensity data were collected at 85 K on a Picker automated four-circle diffractometer. Using Mo Kα radiation, a total of 3568 reflections were collected by a 20-s ω scan of the most intense part of the peak at a scan speed of 0.25° min^{-1} in the range $3.5° < 2\theta < 45°$. A background curve was measured as a function of 2θ. The structure was solved and refined by Patterson, Fourier, and least-squares methods to a final R index[8] of 0.063 using 3339 reflections having $I_{\mathrm{net}} > 2\sigma(I_{\mathrm{net}})$. The positions of the phenyl hydrogens were easily located from a final difference Fourier while the methyl hydrogens were less well-resolved.

The structure of the cation is illustrated in Figure 1. The three palladium atoms are collinear with the two phosphorus atoms of triphenylphosphine groups, forming a five atom chain (since the point group for the molecule is $\bar{1}$, the Pd-Pd-Pd angle is constrained to 180°, the Pd(1)-Pd(2)-P angle is 173.7 (0.1)°). Each palladium atom is coordinated to two methyl isocyanides and exhibits approximate square planar geometry. The square planes are twisted away from each other such that the angle between the two five-atom least-squares planes is 74.5°. The most striking aspects of the structure are the short Pd-Pd bond at 2.5921 (5) Å and the displacement of the equatorial isocyanide towards the center of the molecule. The palladium-palladium bond in $(CH_3NC)_6Pd_2^{2+}$, which is the shortest reported palladium-palladium bond, is just slightly shorter at 2.5310 (9) Å.[9]

The displacement of the equatorial isocyanides towards the center was also observed in $(CH_3NC)_6Pd_2^{2+}$ (av Pd-Pd-C angle = 85.0 (9)°) but occurs to a greater extent in **2** (av Pd-Pd-C = 80.0 (2)°). Although the steric bulk of the axial triphenylphosphine groups could contribute to this large displacement in **2,** it is probably not the sole cause, since normal nonbonded distances between the isocyanides and the phenyl groups are found. The acute Pd-Pd-C angle brings the triply bonded carbon atom of the equatorial isocyanide to within van der Waals distance of the adjacent palladium atom.[10] For example, the Pd(1)- -C(2) distance is 2.921 Å. By contrast, the bonded Pd(2)-C(2) distance is 1.989 (8) Å. We therefore feel it likely that the inward bend of the equatorial isocyanides is in part an electronic effect arising from interaction between filled d orbitals on palladium with empty π^* orbitals on the isocyanide ligands of the adjacent metal. An analogous effect for carbonyl ligands has been termed "semibridging".[11] In the electron-precise metal carbonyl dimers the M-M-C angles