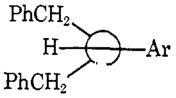
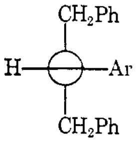
peratures was a typical AB quartet. On raising the temperature, the quartet collapsed reversibly to a singlet in the manner characteristic of protons undergoing a critical rate site exchange on the nmr time scale. Free energies of activation were estimated at the coalescence temperature (T_c) from eq 1 and the Eyring equation;[13] these values and the various nmr parameters are listed in Table I.

$$k_c = \pi(\Delta\nu_{AB}{}^2 + 6J_{AB}{}^2)^{1/2}2^{-1/2} \quad (1)$$

If the benzyl groups were nonequivalent at lower temperatures, the methylene protons in each group remaining equivalent, the spectrum would be a doublet, not a quartet. The observed spectrum therefore indicates that the methylene protons must be nonequivalent. However the benzyl groups *are* equivalent since otherwise one would observe two AB quartets, not one. These observations show either that rotation about the N–N bond must be rapid or that the compounds have the conformation VI where the imino nitrogen is either planar or rapidly inverting (so that it is planar on an average). The nonequivalence of the benzyl protons could then be due either to slow inversion of the adjacent nitrogen atom or slow rotation about the N–N bond coupled with rapid inversion (or planarity) of both nitrogens; in the latter case the structure would be effectively VII.



VI



VII

There is another conceivable way in which asymmetry could arise. In the case of picryl, steric hindrance will probably prevent the phenyl–N–N system from being coplanar. Since rotation about the C–N bond in picramides seems to require considerable activation,[14] the molecule could then exist in two enantiomeric forms, depending on the chirality of the ring relative to the system $(PhCH_2)_2N–NH–C$. Indeed, a second temperature-dependent process was observed in the spectrum of IV in the same temperature range. At 0° the two picryl protons appeared as an AX system ($\Delta\nu_{AX} = 57.3$ Hz; $J_{AX} = 2.7$ Hz)[15] which coalesced at 58° to a broad A_2 system; the corresponding value for $\Delta G^{\ddagger}$ (16.2 kcal/mole) was essentially identical with that for coalescence of the benzyl protons, and similar barriers have been observed[14] in other picramides. This explanation cannot, however, apply in the case of III or V since in both cases the Ar–N–N system can be coplanar; the measured barrier here must refer to nitrogen inversion–rotation.

The fact that the barrier in II is greater than that in a simple amine can be attributed to enhanced repulsion between the nitrogen lone pairs when one of them occupies a p AO instead of a sp^3 hybrid AO; such a situation exists in the transition state for inversion. If both nitrogen atoms were planar, repulsion would then presumably be still greater. Any tendency to coplanarity of one nitrogen atom in hydrazine should therefore tend to increase the barrier to inversion at the other nitrogen, since inversion will involve a transition state in which both nitrogen atoms are coplanar.

One might also expect coplanarity of one or both nitrogen atoms in hydrazine to increase the barrier to rotation for the same reason, the lone-pair repulsions in the transition state for rotation being augmented if the electrons occupy p or π orbitals.

On either basis one could attribute the enhanced barriers in III and V to a resonance interaction between the electrophilic aromatic ring and the imino nitrogen, thus tending to make the nitrogen atom more nearly coplanar than that in II and the barrier to inversion or rotation correspondingly greater.

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[13] See R. J. Kurland, M. B. Rubin, and W. B. Wyse, *J. Chem. Phys.*, **40**, 2426 (1964); M. Oki, H. Iwamura, and H. Hayakawa, *Bull. Chem. Soc. Japan*, **37**, 1865 (1964).

[14] J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, **41**, 1033 (1964).

[15] The overlapping NH signal was removed by deuteration.

Spin Delocalization in Aromatic Complexes of Transition Metals

Sir:

Recently the weaknesses of the Levy–Orgel[1] mechanism for spin delocalization in the metallocenes has been recognized,[2,3] and alternative mechanisms[3–5] have been postulated to explain the observed contact shift data. Rettig and Drago[3] have made a thorough analysis of the data and have proposed a molecular orbital model which is able to explain the observed contact shifts by invoking three competing mechanisms: (1) a pseudocontact mechanism which appears to be negligible except for perhaps chromocene and ferricinium ion; (2) a π mechanism which involves atomic exchange polarization and becomes more important as one goes from vanadocene to nickelocene; and (3) a σ mechanism which delocalizes unpaired spin density directly onto the protons of the ring. In detailed semiempirical calculations[3,6] several workers have noted the importance of σ bonding in what have primarily been considered "π complexes." In fact our calculations show that σ delocalization of spin completely swamps the π-polarization effects for vanadocene and is of approximately equal importance in nickelocene. Fritz, *et al.*,[5] have concurred with our proposal of competing mechanisms but suggest that *direct overlap* of metal orbitals with ring protons of the cyclopentadiene is the dominant mechanism for direct spin delocalization. This mechanism is said to place spin directly on the ring protons without altering the sign of the spin density and leads to the large downfield shifts observed in vanadocene, for example. These authors[5] have suggested this model also accounts for the delocalization of unpaired spin in the series of benzene complexes.

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[1] D. A. Levy and L. E. Orgel, *Mol. Phys.*, **3**, 583 (1961).

[2] M. F. Rettig and R. S. Drago, *Chem. Commun.*, **23**, 891 (1966).

[3] (a) M. F. Rettig and R. S. Drago, *J. Am. Chem. Soc.*, **91**, 1361 (1969); (b) M. F. Rettig and R. S. Drago, *ibid.*, **91**, 3432 (1969).

[4] H. P. Fritz, H. J. Keller, and K. E. Schwarzhans, *Z. Naturforsch.*, **22b**, 891 (1967).

[5] H. P. Fritz, H. J. Keller, and K. E. Schwarzhans, *ibid.*, **23b**, 298 (1968).

[6] A. T. Armstrong, D. G. Carroll, and S. P. McGlynn, *J. Chem. Phys.*, **47**, 1104 (1967).

Table I. Orbital Contributions to ψ Evaluated at Proton Nucleus

Atom	Orbital	Overlap with 1s(H)	Coefficient in a_{1g} MO	Orbital ψ at proton $\times 10^3$	Contribution to $\psi_{total}{}^b \times 10^3$
Cr	$3d_{z^2}$	−0.0036	1.0024	−0.1846	−0.1848
	$3d_{xz}$	0.0146	0.0	0.7524	0.0
	$3d_{x^2-y^2}$	−0.0120	0.0	−0.6179	0.0
	$3d_{yz}$	0.0252	0.0	1.303	0.0
	$3d_{xy}$	0.0207	0.0	0.5351	0.0
	4s	0.1501	−0.0937	13.10	−1.228
	$4p_z$	0.1389	0.0	14.84	0.0
	$4p_x$	0.1140	0.0	12.19	0.0
	$4p_y$	0.1975	0.0	21.11	0.0
C[a]	2s	0.5187	−0.0218	80.07	−1.743
	$2p_z$	0.0	−0.0441	0.0	0.0
	$2p_x$	0.2602	0.0169	68.72	1.161
	$2p_y$	0.4508	0.0292	119.0	3.475
H[c]	1s	1.0	0.0570	741.6	42.20

[a] Only for carbon attached to proton in question. [b] $\psi_{total} = 43.72 \times 10^{-3}$. [c] Cr–H distance is 2.942 A based on inter-ring distance of 3.06 Å for $Cr(C_6H_5CH_3)_2I$: O. V. Starovskii and V. T. Struchkov, *Dokl. Akad. Nauk SSSR*, **135**, 620 (1961).

In our analysis[3b] of the cyclopentadiene complexes we were able to show that the direct "d"-orbital proton overlap contribution to the shift was insignificant, this being one of the many σ effects which is evaluated. It is the purpose of this note to show that this direct overlap effect is also insignificant in the benzene complexes, even when 4s and 4p orbitals on the metal are included.

Since it is claimed that the "direct overlap" mechanism can explain the large downfield shift in bisbenzenechromium(I) cation,[5,7] we decided to carry out an extended Hückel molecular orbital calculation for this species as well as for the neutral bisbenzenevanadium system, which contain one unpaired electron in an a_{1g} molecular orbital, and use the resulting eigenfunction containing the unpaired spin to evaluate ψ^2 at the nucleus of the ring protons. Several workers[8,9] have recently speculated as to the nature of the spin delocalization in transition metal complexes of benzene having noted the failure of the McConnell relationship to explain the observed coupling constants. Our calculation has established the dominance of the σ system in spin delocalization.

We have employed Clementi[10] SCF "double-ζ" functions for carbon 2s and 2p orbitals; Richardson[11] SCF 3d, 4s, and 4p "double-ζ" functions for the metals; and Basch, Viste, and Gray[12] VOIP's for carbon, hydrogen, and metal diagonal matrix elements. An exponent of 1.2 was used throughout for hydrogen. The calculations were insensitive to various off-diagonal approximations employed. Charges were iterated to self-consistency within 0.03 charge unit.

Calculations for $Cr(C_6H_6)_2^+$ give A_H coupling constants in the range +3.0–+5.2 for various metal basis sets (A_H(exptl) = +3.5),[9] and for $V(C_6H_6)_2$, A_H(calcd) in the range +3.1–+4.8 (A_H(exptl) = +4.0).[9] Considering the limitations of the extended Hückel method, we are gratified by these results and have confidence in our wave functions at least with respect to calculation of the coupling constants. The ground states for both $Cr(C_6H_6)_2^+$ and $V(C_6H_6)_2$ are predicted to be A_{1g} which are in agreement with previous assignments[13,14] and with the magnetic moments which are very close to the spin-only moment of 1.73. Our calculation further shows that both the 4s and 4p orbitals on the metal are essentially virtual.

Since the electron–nuclear coupling constant A_H is dependent on the value of ψ^2 from the Fermi-contact relationship, we have tabulated (see Table I) the contributions to ψ arising in the fragment Cr–C–H for simplicity; other orbital contributions to the value of ψ at the hydrogen atom nucleus of this fragment are small. Considering the Cr–H distance of 2.942 Å, the 3d orbitals of chromium are not expected to give very large overlaps with the hydrogen 1s orbital since the radial portion of the Richardson 3d "double-ζ" function is maximum at about 0.4 Å from the metal and tails off quite rapidly. The radial portion of the 4s function peaks at 2.2 Å and, as expected, its overlap increases. The diffuse 4p orbital peaks at around 3.3 Å and also gives appreciable overlap with the hydrogen 1s orbital. However, since the 4p orbital coefficients in the a_{1g} orbital of $Cr(C_6H_6)_2^+$ are zero, these orbitals *make no* contribution to ψ at the proton. On the other hand, the 4s orbital makes a *negative* contribution to ψ about the same order of magnitude as that of the 2s orbital of the carbon atom. It is obvious that the contribution to ψ from the proton itself completely dominates, just as it did for the metallocenes.[3] We have now shown that direct overlap with metal orbitals including 4s and 4p is not important to the over-all σ spin delocalization mechanism which apparently operates.

In conclusion, our molecular orbital calculation is able to reproduce well the experimental coupling constants for $Cr(C_6H_6)_2^+$ and $V(C_6H_6)_2$. We have further shown by actual evaluation of ψ at the proton nucleus that the metal orbitals make very little contribution to ψ by a "direct overlap" mechanism, such

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(7) Y. S. Karimov, V. M. Tschibrikin, and I. F. Schtschegolev, *J. Phys. Chem. Solids*, **24**, 1683 (1964).

(8) R. D. Feltham, P. Sogo, and M. Calvin, *J. Chem. Phys.*, **26**, 1354 (1957).

(9) (a) G. Henrici-Olive and S. Olive, *Z. Physik. Chem.* (Frankfurt), **56**, 223 (1967). (b) Since submitting this communication, we have shown A_H = +4.1 ± 0.1 G from the wide-line nmr spectrum of $V(C_6H_6)_2$.

(10) E. Clementi, "Tables of Atomic Functions," IBM Corp., San Jose, Calif., 1965.

(11) N. W. Richardson, W. C. Niewport, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962); **38**, 796 (1963).

(12) H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta*, **3**, 458 (1965).

(13) R. D. Fischer, *ibid.*, **1**, 418 (1963).

(14) (a) E. Schustorovitch and M. E. Dyatkina, *Dokl. Akad. Nauk SSSR*, **128**, 1234 (1959); (b) R. Prins and F. J. Reinders, *Chem. Phys. Lett.*, **3**, 49 (1969).

as has been postulated.[4,5,7] Instead, the ring σ molecular orbital is extensively delocalized and has large proton coefficients. Overlap of the metal orbitals with this extensively delocalized molecular orbital is the mechanism which distributes unpaired spin over the protons. The spin is placed on the atoms in the benzene in proportion to the atomic orbital coefficients in the molecular orbitals *which contain the unpaired spin.* We are extending our calculations to consideration of delocalization in other complexes of transition metals with aromatic ligands.

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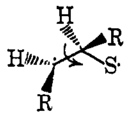
The Nature of the Intermediates in the Sensitized *cis–trans* Photoisomerization of Alkenes

Sir:

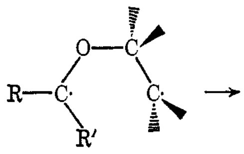
Two mechanisms have been proposed to account for *cis–trans* photoisomerization which results when simple olefins interact with triplet states of sensitizers: the Schenck mechanism involving formation of an adduct diradical, **1**, in which rotation about the central bond



$$\longrightarrow \mathrm{S} + \alpha\,{}^{0}t + (1-\alpha)\,{}^{0}c \qquad (1)$$

1

is rapid relative to bond breaking (eq 1),[1] and the triplet mechanism in which olefin triplets are formed by excitation transfer from the sensitizer.[2,3] The triplet mechanism is favored when the excitation transfer steps are exothermic. To account for isomerization in cases where the sensitizer triplet excitation energy is not sufficient to excite the olefins to planar (spectroscopic) triplet states, nonvertical excitation transfer leading directly to twisted olefin triplet has been suggested.[4–6] For the case of carbonyl sensitizers with lowest n–π^* triplet states formation of the Schenck intermediate has been proposed as a discrete step in the excitation transfer process (eq 2).[7] The following observations provide an experimental criterion for choosing between the Schenck and the triplet mechanisms.



$$\longrightarrow \mathrm{RR'C{=}O} + {}^{3}[\text{olefin}] \qquad (2)$$

2

The simplest general scheme for sensitized *cis–trans* photoisomerization is given by eq 3–7, where *X represents an unspecified common intermediate, and other symbols have their usual meanings.[2] Steady-state approximations for ^{3}S and *X lead to eq 8–10.[2] Equation 8 represents the photostationary *trans/cis* ratio,

$$ {}^{0}\mathrm{S} \xrightarrow{h\nu} {}^{1}\mathrm{S} \longrightarrow {}^{3}\mathrm{S} \qquad (3)$$

$$ {}^{3}\mathrm{S} \xrightarrow{k_4} {}^{0}\mathrm{S} \qquad (4)$$

$$ {}^{3}\mathrm{S} + {}^{0}t \xrightarrow{k_5} {}^{*}\mathrm{X} \qquad (5)$$

$$ {}^{3}\mathrm{S} + {}^{0}c \xrightarrow{k_6} {}^{*}\mathrm{X} \qquad (6)$$

$$ {}^{*}\mathrm{X} \xrightarrow{k_7} \alpha\,{}^{0}t + (1-\alpha)\,{}^{0}c \qquad (7)$$

$$([t]/[c])_{\mathrm{s}} = (k_6/k_5)[\alpha/(1-\alpha)] \qquad (8)$$

$$\frac{1}{\phi_{t\to c}} = \frac{1}{1-\alpha}\left(1 + \frac{k_4}{k_5[t]}\right) \qquad (9)$$

$$\frac{1}{\phi_{c\to t}} = \frac{1}{\alpha}\left(1 + \frac{k_4}{k_6[c]}\right) \qquad (10)$$

and eq 9 and 10 give the dependence of *trans* → *cis* and *cis* → *trans* quantum yields on initial concentrations of *cis* and *trans* isomers.[8]

The dependence of *trans/cis* photostationary ratios for several olefins on the triplet energies of sensitizers has been attributed entirely to changes in the excitation ratio k_6/k_5.[2,11,12] Direct measurements of rate constants k_6 and k_5 have confirmed this interpretation for the stilbenes and the 1,2-diphenylpropenes.[5] For these olefin pairs photostationary state ratios could be predicted using a *single decay ratio*, $\alpha/(1-\alpha)$, in each case.[5]

Benzene-sensitized photoisomerization of alkenes has been studied in the vapor phase[3] and in solution.[12,13] Stationary states for several alkene pairs are close to unity. Since triplet excitation transfer should be, in all cases, at least 2–3 kcal/mole exothermic, k_6/k_5 is expected to be close to unity;[2] hence, for *X = ^{3}[alkene], $\alpha/(1-\alpha) = 1.0$.[14]

We have studied the *cis–trans* photoisomerization of the 2-pentenes using acetone and acetophenone as sensitizers.[15] The results are in accord with eq 9–10

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[1] G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, **71**, 781 (1962).

[2] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

[3] E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968), and references cited therein.

[4] G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2516 (1963).

[5] W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

[6] *Cf.*, however, A. Bylina, *Chem. Phys. Lett.*, **1**, 509 (1968).

[7] N. C. Yang, J. L. Cohen, and A. Shani, *J. Am. Chem. Soc.*, **90**, 3264 (1968); *cf.*, also, R. A. Caldwell and G. W. Sovocool, *ibid.*, **90**, 7138 (1968), and S. M. Japar, M. Pomerantz, and E. W. Abrahamson, *Chem. Phys. Lett.*, **2**, 137 (1968).

[8] Side reactions, *e.g.*, oxetane formation, have been neglected. The efficiency of intersystem crossing for the sensitizer was taken as unity. The latter is a valid assumption for acetophenone[9] and acetone.[10] Oxetane formation is a minor reaction in the case of acetophenone, and its quantum yield does not depend on the pentene isomer used. Step 4 includes reactions with solvent.

[9] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 2129 (1965).

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[12] M. A. Golub and C. L. Stephens, *ibid.*, **70**, 3576 (1966).

[13] M. A. Golub, C. L. Stephens, and J. L. Brash, *J. Chem. Phys.*, **45**, 1503 (1966).

[14] The best experimentally determined value seems to be $\alpha/(1-\alpha) = 1.00 \pm 0.10$ for the 2-butenes.[3]

[15] Benzophenone-sensitized *trans* → *cis* photoisomerization of the piperylenes was used for actinometry.[9] Irradiations were carried out at 30° in a merry-go-round apparatus using the 3130-Å Hg line. In the case of acetone, the sensitizer was used as solvent; in the case of acetophenone solutions were 0.057 *M* in sensitizer, and cyclohexane was used as solvent. In calculating quantum yields the results were corrected for back reaction.[9] Analyses were by glpc using a 50 ft × 1/8 in. column packed with 20% $\mathrm{AgNO_3}$ in ethylene glycol on Firebrick.