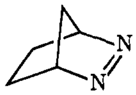
using at least five different quencher concentrations.[16] The measured quenching rate constants are listed in Table I.

Table I. Rate Constants for Quenching of Triplet Triphenylene[a]

Quencher	Rate constant, M^{-1} sec^{-1} [b]
trans-Stilbene[c]	6×10^9
Azo-*n*-butane	6×10^9
Azoisobutane	3×10^9
Azo-*sec*-butane	6×10^8
Azo-1-adamantane	6×10^8
Azo-*tert*-butane	3×10^8

[a] In benzene solution at room temperature; measured triphenylene triplet lifetime 1×10^{-4} sec. [b] Estimated error limits ±20%. [c] This case represents the diffusion-controlled rate previously measured to be 7×10^9 M^{-1} sec^{-1}; see ref 4.

The quenching rates clearly drop sharply as substitution is increased about the azo functional group. A completely diffusion-controlled rate is observed only with azo-*n*-butane, and the quenching rates steadily decrease as the alkyl substituents proceed from primary to secondary to tertiary. Except perhaps for azo-1-adamantane, the observed rate constants correlate extremely well with what would be expected purely on the basis of steric effects. The rate of quenching of triplet triphenylene by a cis azo compound, 2,3-diazabicyclo[2.2.1]heptene-2 (**1**) (E_T = 60 kcal/mol), has been determined to be 3×10^9 M^{-1} sec^{-1} in benzene solution.[18] Although the azo functional group in **1** is attached to secondary substituents, the cis stereochemistry almost certainly renders the chromophore more accessible than the trans stereochemistry of the corresponding azo-*sec*-butane.



1

Based upon Dexter's theoretical formulation of electron-exchange energy transfer,[19] it has been calculated that triplet energy transfer rates should fall off one order of magnitude for each 1.2 Å increase in separation between the donor and acceptor chromophores.[10,20] Molecular models and calculations indicate that a tertiary substituent, such as *tert*-butyl or 1-adamantyl, possesses a van der Waals radius which would extend about 1 Å beyond that of a π system.[10] Thus, triplet energy transfer from triphenylene to azo-*n*-butane proceeds at a diffusion-controlled rate because the donor and acceptor chromophores may come into direct contact, but triplet energy transfer from triphenylene to azo-*tert*-butane occurs at a rate one order of magnitude less than diffusion-controlled because the tertiary substituents keep the donor and acceptor chromophores (van der Waals radii) separated by about 1 Å. The specific orientation which leads to this prediction involves the azo compound lying flat over the plane of the triphenylene molecule.

The rate of singlet energy transfer from triphenylene to azo-*tert*-butane has been determined both by fluorescence lifetime quenching and by fluorescence intensity quenching to be 5.6×10^9 and 6.2×10^9 M^{-1} sec^{-1}, respectively.[13] Since this rate constant is at the diffusion-controlled limit, it would appear that steric hindrance is substantially less important in the transfer of singlet electronic excitation in solution.[21,22]

We are currently determining the rates of quenching of lower energy sensitizer triplet states by the same series of azo compounds, in order to ascertain the effect of energetics upon the magnitude of these steric effects.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for generous support of this work.

---

[16] Although the subject of energy transfer to azo compounds has been the source of substantial confusion,[13,17] the method of monitoring triplet decay rates assures that we are observing only triplet quenching.

[17] P. D. Bartlett and P. S. Engel, *J. Amer. Chem. Soc.*, **90**, 2960 (1968).

[18] These experiments were performed by C. C. W. under conditions identical with those reported herein; cited by P. S. Engel, *ibid.*, **91**, 6903 (1969).

[19] D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

[20] B. Smaller, E. C. Avery, and J. R. Remko, *ibid.*, **43**, 922 (1965).

[21] A. Yekta and N. J. Turro, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, Abstract PHYS-53.

[22] Steric hindrance is important in vapor-phase singlet energy transfer, however: K. Janda and F. S. Wettack, *J. Amer. Chem. Soc.*, **94**, 305 (1972).

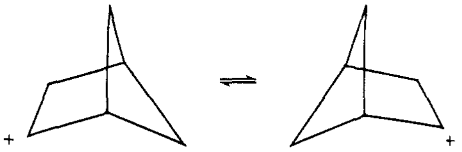
Carl C. Wamser,* Peter L. Chang
Department of Chemistry, California State University, Fullerton
Fullerton, California 92634

Received August 29, 1972

Nature of the 2-Bicyclo[2.1.1]hexyl Cation[1]

Sir:

It is commonly observed that cyclobutylcarbinyl derivatives rearrange on solvolysis to cyclopentyl compounds.[2] A particularly interesting example of this type of rearrangement is found with bicyclo[2.1.1]hexyl-2 derivatives for here the rearranged ion is degenerate with the unrearranged ion (eq 1). This case has been studied by Meinwald and Gassman[3] and by Meinwald and Crandall.[4] They have presented evidence showing a rearrangement of the type shown above and found the rate of solvolysis to be greater than might be expected for simple open ions. This led to the suggestion that the species formed on ionization might be a bridged ion (eq 2).



(1)

This appeared to be a case in which a stable ion or equilibrating group of ions might be found. Thus, the reaction of 2-chlorobicyclo[2.1.1]hexane[5] with antimony

---

[1] This investigation was supported by grants from the National Institutes of Health and the National Science Foundation.

[2] *Cf.* R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 278.

[3] J. Meinwald and P. G. Gassman, *J. Amer. Chem. Soc.*, **85**, 57 (1963).

[4] J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966).

[5] The chloride was prepared from bicyclo[2.1.1]hexan-2-ol[6] by the reaction with thionyl chloride. Its properties were identical with those of material prepared by a different method.[7]

[6] F. T. Bond, H. L. Jones, and L. Scerbo, *Tetrahedron Lett.*, 4685 (1965).

[7] R. Srinivasan and F. I. Sonntag, *J. Amer. Chem. Soc.*, **89**, 407 (1967).

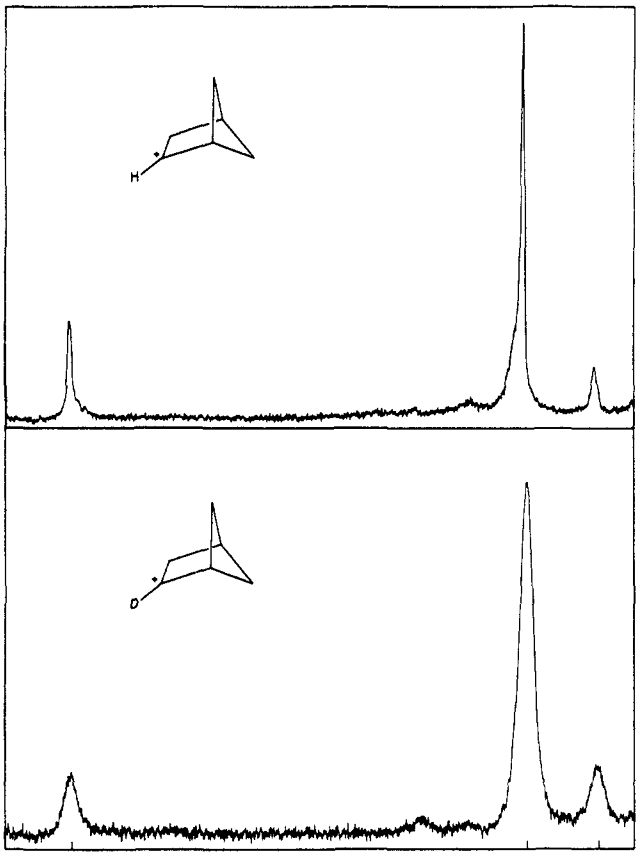
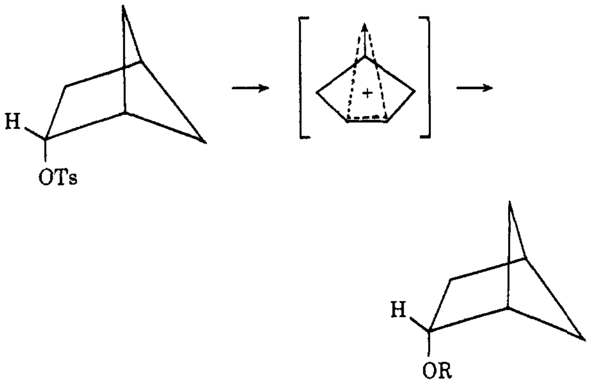


Figure 1. Nmr spectra of the bicyclo[2.1.1]hexyl-2 cation (upper curve) and its 2-deuterio derivative (lower curve).

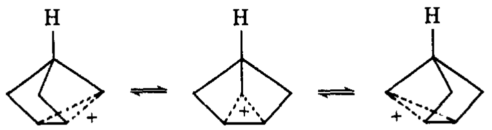


(2)

pentafluoride in sulfuryl chlorofluoride was examined at −125°. The nmr spectrum of the solution (Figure 1) had three single peaks at δ 8.32 (2 H), 3.70 (6 H), and 2.95 (1 H). No line broadening was observed in the temperature range −90 to −130°. When 2-chlorobicyclo[2.1.1]hexane-2-d_1[8] was used, the same spectrum was observed, except that the δ 8.32 peak corresponded in area to only one proton.

These data indicate that the six methylene protons become equivalent on the nmr time scale even at −130° and show that hydrogen shifts do not occur at an appreciable rate at temperatures as high as −90°. Assuming a value of $\Delta S^{\ddagger} \approx 0$, the activation enthalpy for the methylene group equilibration must be less than 7 kcal/mol and the activation enthalpy for the possible hydrogen shift is greater than 13 kcal/mol.

The minimum activation enthalpy for hydrogen migration is considerably higher than that for a typical rearrangement in a system in which open carbonium ions are expected (<5 kcal/mol).[9] This, coupled with the low activation enthalpy for methylene equilibration, strongly suggests that the observed rearrangement is between a group of bridged ions[10] (eq 3). CNDO[11]



(3)

calculations for this system suggest that the activation energy for the rearrangement should be quite low. The bridged structure would be expected to lead to a relatively low rate of hydrogen migration from a methylene group to a cationic center.[12]

Solvolysis of the tosylate derived from bicyclo[2.1.1]hexan-2-ol-2-d_1 led to bicyclo[2.1.1]hexyl-2 acetate in which the deuterium was equally distributed between the alcohol carbon and the adjacent bridgehead position. This is in good accord with the nmr data.

The apparent rearrangement of one bridged ion to another is of particular interest in connection with the "memory effect" which Berson[13] observed in a number of solvolytic reactions. One good interpretation of these effects involves the transformation of one bridged ion into another, thereby preserving stereochemical information concerning the origin of the ions.

When the solutions of the bicyclo[2.1.1]hexyl-2 cation were kept at −97°, a slow rearrangement to the cyclohexenyl cation was observed [δ 10.18 (2 H, d, J = 7.6), 8.22 (1 H, t, J = 7.6), 3.70 (4 H, t, J = 6.7), and 2.42 (2 H, quint, J = 6.7)). A rate constant of (1 ± 0.2) × 10^{-4} sec^{-1} was found. At a higher temperature, the ion rearranged to the methylcyclopentyl cation (k =

---

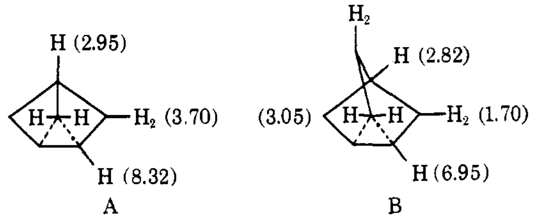
[8] Prepared by the reduction of bicyclo[2.1.1]hexan-2-one[6] with lithium aluminum deuteride followed by treatment with thionyl chloride. Several methods for the conversion of the alcohol to the chloride were tried, but all led to partial rearrangement to the 5-deuterio derivative. This has, however, no effect on the results described.

(9) G. A. Olah, J. R. DeMember, A. Commeyras, and J. L. Brides, *J. Amer. Chem. Soc.*, **93**, 459 (1971); D. M. Brouwer and J. A. van Doorn, *Recl. Trav. Chim. Pays-Bas*, **89**, 88 (1970); H. Hogeveen and C. J. Gaasbeek, *ibid.*, **88**,1305 (1969).

(10) The corresponding 1,2-hydrogen shift also is slow with the norbornyl cation (M. Saunders, P. v. R. Schleyer, and G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 5680 (1964)) for which a similar argument is made. *Cf.* G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3956 (1969).

(11) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); **44**, 3289 (1966).

(12) A comparison of the chemical shifts for the bicyclo[2.1.1]hexyl-2



and norbornyl[11] cations is of interest. Whereas the bridgehead protons have about the same chemical shift in both ions, the other CH protons are found at considerably lower field in A than in B. Since the methylene protons in A are still being equilibrated at the lowest temperature of observations, they might be expected to be found at the weighted average of the corresponding protons in B (*i.e.*, (2 × 1.70 + 3.05)/3) or δ 2.2. Again, they are found at lower field than expected. The change in geometry for the protonated cyclopropane group in the two ions clearly has an important effect on the chemical shifts.

(13) J. A. Berson, *et al.*, *J. Amer. Chem. Soc.*, **91**, 5550, 5567, 5580, 5594, 5601 (1969).

$(1.4 \pm 0.2) \times 10^{-4}$ sec^{-1} at 11 ± 3°). The nmr spectrum had bands at δ 10.38 (1 H, m), 8.16 (1 H, d, $J = 3$), 3.9 (2 H, m), 3.8 (2 H, m), and 3.4 (3 H, m), which is comparable to that reported by Winstein for this ion.[14,15]

The use of 2-chlorobicyclo[2.1.1]hexane-*2-d*$_1$ as the reactant led at −75° to a 1:1 mixture of 1-deuteriocyclohexenyl and 2-deuteriocyclohexenyl cations. At −65°, the deuterium begins to scramble about the cyclohexenyl ring. The ratio of the areas of the δ 10.18 and 8.22 bands changed from 3 to 2. Complete scrambling of the label was achieved after 6–10 hr at −65°.

---

(14) Dr. Philip Warner, private communication.

(15) The cyclohexenyl cation to methylcyclopentenyl cation has received considerable study in alkyl substituted cases: N. C. Deno and J. J. Houser, *J. Amer. Chem. Soc.*, **86**, 1741 (1964); N. C. Deno and R. R. Lastomirsky, *ibid.*, **90**, 4085 (1968); T. Sorensen, *ibid.*, **89**, 3782, 3794 (1967); **91**, 6398 (1969); T. Sorensen and K. Ranganayakulu, *ibid.*, **92**, 6539 (1970).

Gunther Seybold, Pierre Vogel
Martin Saunders, Kenneth B. Wiberg*
Department of Chemistry, Yale University
New Haven, Connecticut 06520

Received July 17, 1972

Use of $^1|J_{^{195}\mathrm{Pt}-^{15}\mathrm{N}}|$ as a Probe into the Electronic Structure of Some Platinum(II)–Amine Complexes

Sir:

The question of the extent of π bonding in square-planar platinum(II) complexes remains a subject for considerable debate. Although the concept of "back-bonding" between platinum 5d orbitals and suitable ligand orbitals has frequently been invoked to explain most static and dynamic phenomena in transition metal chemistry including the kinetic trans effect[1] and certain infrared[2] and bond-length data,[3] the data obtained to date have failed to give an unambiguous answer to this problem.

Among the π interactions most frequently postulated are those between phosphorus 3d orbitals and metal d orbitals. Of particular interest in this context have been the efforts to correlate $^1|J_{^{195}\mathrm{Pt}-^{31}\mathrm{P}}|$ coupling constants with the extent of π-bond formation between these two nuclei.[4-6] From such data, Pidcock, *et al.*,[6] concluded that the very large differences in coupling constants between cis and trans platinum(II) complexes were due to differences in s character of the hybrids used by the platinum atom to form bonds to the phosphorus atom. These conclusions are supported by extended Huckel MO calculations.[7] The question at issue here is whether or not such changes occur as a consequence of the formation of d_π–d_π bonds. Thus, it seemed desirable to establish the extent of rehybridization accompanying cis–trans isomerization in systems in which the donor–acceptor bond does not have a significant π component.

In an effort to obtain an answer to this question, we have measured the ^{15}N nmr spectra of some complexes of platinum(II) with *n*-dodecylamine (A) labeled with >95 atom % ^{15}N ($I = ^1/_2$). It was thought that a study of the changes in $^1|J_{^{195}\mathrm{Pt}-^{15}\mathrm{N}}|$ for a variety of platinum–amine complexes, relative to some phosphine analogs, might prove revealing. The choice of the amine as well as the degree of enrichment were dictated by the need for relatively high concentrations of ^{15}N.[8] The observed $^1|J_{^{195}\mathrm{Pt}-^{15}\mathrm{N}}|$ coupling constants are shown in Table I.

Table I. $^1|J_{^{195}\mathrm{Pt}-^{15}\mathrm{N}}|$ Coupling Constants in Some Platinum Complexes of *n*-Dodecylamine (A)

No.	Compound	J^a	$J_{\mathrm{cis}}/J_{\mathrm{trans}}$
1	*cis*-[$\mathrm{PtCl_2A_2}$]	351	1.21
2	*trans*-[$\mathrm{PtCl_2A_2}$]	290	
3	*cis*-[$\mathrm{PtBr_2A_2}$]	334	1.20
4	*trans*-[$\mathrm{PtBr_2A_2}$]	279	
5	*cis*-[$\mathrm{PtCl_4A_2}$]	249	
6	*cis*-[$\mathrm{PtBr_4A_2}$]	223	
7	[$\mathrm{PtBrA_3}$]Br	342^b	
		288^c	1.19
8	[$\mathrm{PtA_4}$]$\mathrm{Br_2}$	298	

^{a} Measured as saturated solutions in chloroform. The data are estimated to be correct to ±2 Hz. ^{b} For the nitrogen atom in a trans position to bromine. ^{c} For the nitrogen atoms in trans positions to each other.

The data can be interpreted in terms of the theory developed by Ramsay[9] which assumes the dominance of the Fermi contribution. Using the equation of Pople and Santry[10] for the directly bonded X–Y coupling in a covalent bond, one can write the expression for the term $^1|J_{^{195}\mathrm{Pt}-^{15}\mathrm{N}}|$ in an abbreviated form as

$$^1|J_{^{195}\mathrm{Pt}-^{15}\mathrm{N}}| \propto (\Delta E)^{-1}\alpha_{\mathrm{Pt}}{}^2\alpha_{\mathrm{N}}{}^2|\psi_{\mathrm{Pt}(6s)}(0)|^2|\psi_{\mathrm{N}(2s)}(0)|^2$$

where ΔE is an average excitation energy, $\alpha_{\mathrm{X}}{}^2$ is the s character of the hybrid used by X in the platinum–nitrogen bond, and $|\psi_a(0)|^2$ is the electron density of orbital a evaluated at the nucleus. As found for the phosphorus complexes examined earlier,[6] there is no correlation between the Pt–N coupling constants and the parameter ΔE.[11] Thus, it appears that the coupling is directly proportional to terms involving the s character of the bonding orbitals. A similar approach has been suggested for ^{15}N and has been shown to be valid for the ^{15}N-H bond in a series of aniline derivatives.[12] Such correlations have also been suggested[13] for other nuclei, *e.g.*, the $^1|J_{^{195}\mathrm{Pt}-^{13}\mathrm{C}}|$ is responsive in a predictable manner to the s character of the carbon atom. In this

---

(1) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955); L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, and references therein.

(3) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Crystallogr.*, **13**, 149 (1960).

(4) J. F. Nixon and A. Pidcock in "Annual Review of NMR Spectroscopy," Vol. 2, E. Mooney, Ed., Academic Press, London, 1969, p 345.

(5) S. O. Grim, R. L. Keiter, and W. McFarlane, *Inorg. Chem.*, **6**, 1133 (1967).

(6) A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966).

(7) S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6669 (1968).

(8) $I = ^1/_2$, natural abundance = 0.36%. The more abundant isotope (I = 1, natural abundance = 99.64%) possesses a quadrupole moment which frequently prohibits accurate measurements of the desired spin–spin interactions.

(9) N. F. Ramsay and E. M. Purcell, *Phys. Rev.*, **85**, 143 (1952); N. F. Ramsay, *Phys. Rev.*, **91**, 303 (1953).

(10) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(11) This is based on the assumption that the lowest energy electronic transitions are primary in determining the magnitude of ΔE and on the observation that such transitions show a trend which is opposite to that of the observed coupling constants.

(12) M. B. Bramwell and E. W. Randall, *Chem. Commun.*, 250 (1969); T. Axenrod, P. S. Pregosin, M. J. Wieder, and G. W. A. Milne, *J. Amer. Chem. Soc.*, **91**, 3681 (1969).

(13) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *Chem. Commun.*, 1627 (1971).