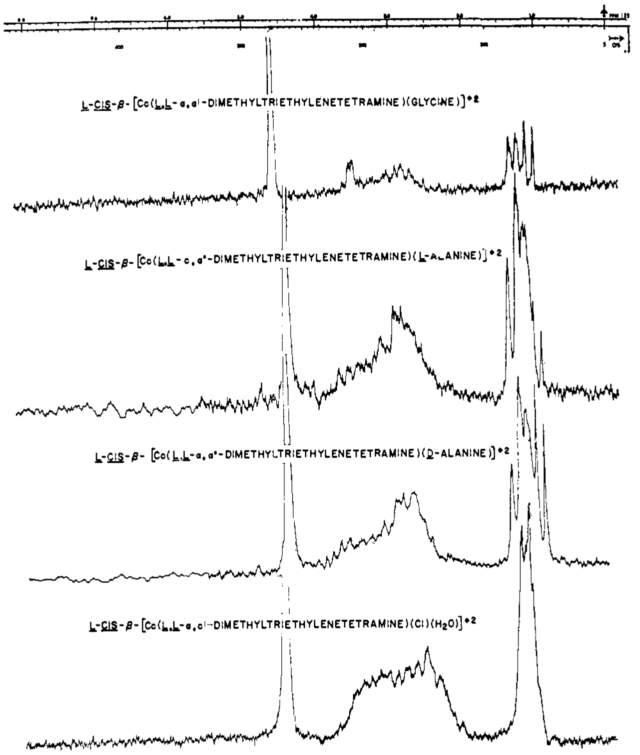

Figure 2. Nmr spectra.

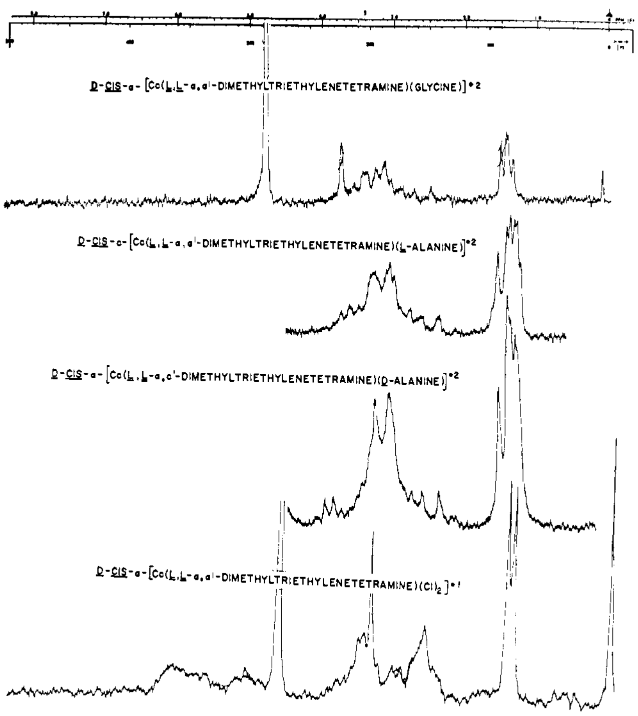

Figure 3. Nmr spectra.

dynamic instability expected for the D-*cis*-β[7] isomer. The L-*cis*-β absolute configurations are similarly assigned. The nmr spectra (Varian A-60;[11] ≈0.005 g/0.1 cc of D_2O; ambient temperatures of probe ≈33°; scans taken after samples stood at room temperature for 1–2 hr; all exchangeable protons were lost; external standard, NaTMS) are shown in Figures 2 and 3. It can be seen that every *cis*-β isomer has a characteristic methyl doublet, $J = 6.5$ cps, shifted upfield from the remaining methyl resonance peaks (Figure 2 and Table I). This doublet is absent in the *cis*-α isomers of Figure 1d–f as is shown in the nmr spectra of Figure 3. This difference permits the distinction between the α and β configurations whenever the L,L or D,D form of α,α'-dimethyltrien is used as a tetradentate ligand. Owing to the stereopreference of the optically active ligand,[7] the α and β isomers formed from one particular enantiomer of the ligand acquire opposite chirality with respect to the central metal atom. In the case of the L,L ligand the *cis*-β complexes exhibit a negative Cotton effect and are assigned the L absolute configuration [in analogy with $(-)_{546}$-$(Co(en)_2gly)^{2+}$],[8] whereas the *cis*-α complexes exhibit a positive Cotton effect and are assigned the D absolute configuration.

Table I

D-*cis*-α complex	Upfield methyl doublet, τ
D-Alanine	8.85
L-Alanine	8.89
Glycine	8.82

Thus, the assignment of absolute configurations for these stereospecific complexes can be made quickly and easily by noting the pattern of the nmr methyl region. This ability is very important to the development of fundamental knowledge of inorganic reaction mechanism and ligand conformational effects.

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(11) The solutions were prepared in a microcell; scans were on the "Dog" mode of the time-averaging attachment by Dow Chemical Co., Midland, Mich.

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A Correlation between the Triplet State Lifetime and Electronic Polarizability

Sir:

During recent years, lifetime measurements of triplet decay in aromatic compounds have received considerable attention.[1] Many of these triplet lifetimes have been obtained by phosphorescent emission studies carried out in rigid glass solutions at low temperatures. Under these experimental conditions the decay of the triplet molecules usually follows first-order kinetics.[2]

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(1) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

(2) R. G. Bennett, R. P. Schwenker, and R. E. Kellogg, *J. Chem. Phys.*, **41**, 3040 (1964).

In other media and at somewhat higher temperatures, nonexponential decay has been reported.[3]

We have studied triplet-state lifetimes also in random matrix but under conditions in which the temperature could be varied from *ca.* 100°K down to 3.0°K.[4] For simple aromatic molecules the lifetimes vary with temperature in generally the same way. At 80°K the nonradiative processes predominate and the emission is small; at 60° or so, the emission process becomes increasingly important at the expense of viscosity-related quenching processes[5] and, finally, at about 15°K the rates of decay do not change with temperature. These "adiabatic" rates are the subject of this communication and will be referred to simply as the triplet-state lifetimes. The compounds investigated were toluene, *p*-xylene, *p*-diethylbenzene, anisole, diphenyl ether, *p*-ethyltoluene, and ethylbenzene. Approximately 10^{-3} *M* solutions in a 9:1 mixture of methylcyclohexane–isopentane were studied over the temperature range of 3 to 110°K.

The triplet-state lifetime, as defined above, is dependent on at least two terms, the rate of emissive decay and the rate of an "internal quenching" process. The latter type of decay has been discussed by various authors,[6,7] and the relative magnitudes of the two in different types of molecules will probably continue to be debated for some time. Both processes are undoubtedly dependent on molecular structure and matrix interactions and most probably on such minor factors as intermolecular association, some ordering of the matrix liquid structure, and, perhaps, even "surface ordering" of the molecules receiving the largest amounts of exciting radiation. Of these, molecular structure seems to play the most important role, but little is known experimentally about which molecular parameters are of great influence—excepting the effects of large spin–orbit coupling atoms. We are now able to report an empirical relationship between the triplet-state lifetime and the electronic polarizability of the molecules indicated above. A plot of these two parameters is shown in Figure 1.

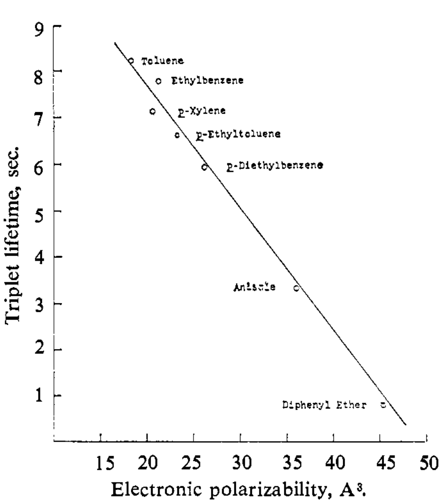

Figure 1. Electronic polarization *vs.* triplet lifetime.

Even though Figure 1 indicates a definite correlation between electronic polarizability and triplet lifetime, these terms are probably not independently related. How a measure of ground-state orbital distortion under the influence of an electric field can be directly related to the "forbiddenness" of a triplet–singlet transition has thus far escaped us. Intuitively, one suspects that both may be related to orbital mixing terms, but no uncontestable arguments can be presented.

These preliminary results suggest that future studies should include examination of other types of molecules with various functional groups, as well as an examination of the effects of heavy atoms, such as the halogens, which have rather large spin–orbit coupling factors, to determine the generality of this correlation.[8]

Acknowledgment. The authors wish to acknowledge the financial support (Grant P-058) of the Robert A. Welch Foundation and helpful discussion with R. G. Parr, W. H. Watson, and H. F. Hameka.

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[3] N. Hirota and C. A. Hutchinson, Jr., *J. Chem. Phys.*, **42**, 3869 (1965).

[4] Employing an Air Products Helium Cryotip refrigeration device.

[5] S. J. Ladner and R. S. Becker, *J. Chem. Phys.*, **43**, 3344 (1965).

[6] G. Robinson and R. Frosch, *ibid.*, **38**, 1187 (1963); G. Robinson and R. Frosch, *ibid.*, **37**, 1962 (1962).

[7] M. Gouterman, *ibid.*, **36**, 2846 (1962).

[8] A detailed description of our experimental procedures and theoretical speculations are available on request.

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Stable Carbonium Ions. XXX.[1] The *p*-Anisonium and 2,4,6-Trimethylphenonium Ions

Sir:

No direct observation of phenonium ion formation *via* phenyl participation from phenylethyl[2] or related systems (anthrylethyl[3]) in strong acid solutions has been achieved so far.

Phenylethyl cations, like the 3-phenyl-2-butyl cation, rearrange in strong acid systems (SbF_5–SO_2, FSO_3H–SbF_5–SO_2) to the more stable benzylic cations, with no evidence of bridged phenonium ion formation.[2]

The observation by Eberson and Winstein[3] of the bridged anthrylethyl cation was achieved not by the aryl-participation route, but indirectly by ionization of the spirocyclopropyl alcohol.

We wish now to report the first direct (nmr spectroscopy) observation of phenonium ion formation *via* aryl participation, that of the *p*-anisonium (I) and 2,4,6-trimethylphenonium (II) ions. Whereas our previous attempts to this effect[4] proved to be unsuccessful on closer reinvestigation,[2] we feel that evidence presented in this communication will stand up to any scrutiny and will provide conclusive evidence for phenonium ion formation *via* phenyl participation in strong acid solution.

Taking advantage of the known powerful participating effect of the *p*-anisyl[5] and mesityl group, we were

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[1] Part XXIX: G. A. Olah, N. Friedman, J. M. Bollinger, and J. Lukas, *J. Am. Chem. Soc.*, **88**, 5329 (1966).

[2] G. A. Olah, C. U. Pittman, E. Namanworth, and M. B. Comisarow, *ibid.*, **88**, 5571 (1966).

[3] L. Eberson and S. Winstein, *ibid.*, **87**, 3506 (1965).

[4] G. A. Olah and C. U. Pittman, *ibid.*, **87**, 3509 (1965).

[5] (a) S. Winstein, *et al.*, *ibid*, **74**, 1140 (1952); **75**, 147 1953; **78**, 328 (1956); see also (b) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Schepple, *ibid.*, **89**, 370 (1967).