anisms for luminescence from these systems. If the interpretation given above is valid, and one sees magnetic field effects only when the triplet route is predominantly responsible for luminescence, then the zero (or very slight) effect observed with the TPP anion–cation reaction implies that the singlet route is much the predominant pathway to luminescence and the reaction is essentially energy sufficient. Such a suggestion is indeed quite plausible, and the energetics may only appear marginal because $-\Delta H^\circ$ has been significantly underestimated (*vide supra*). In contrast, our hypothesis suggests that luminescence from the rubrene anion–cation annihilation arises predominantly from the triplet pathway. Interestingly, Maloy and Bard made the same suggestion as a consequence of their observation of a low emission efficiency from this system compared to that from the DPA anion–cation reaction.[32] Chang, Hercules, and Roe likewise concluded from their analysis of intensity–decay curves that the triplet pathway was an important route to emission from the rubrene anion–cation reaction,[33] and recent work by Bezman and Faulkner using an extended Feldberg analysis has implied that it is the only route.[34] An intriguing issue raised in this work concerns the sharpness of the energy criterion. One wonders whether the line between energy sufficiency and energy deficiency is as distinct and important as these last two cases may suggest. In the marginal energy region it may in fact be that more specific system factors, such as relative geometries of the ions, the excited singlets, and the triplets, become extremely important for dictating the predominant luminescent pathway.

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Temperature-Dependent ^{13}C Relaxation Studies of Small Molecules

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Abstract: ^{13}C spin-lattice relaxation times (T_1) are reported for 60% enriched samples of CH_3OH, CH_3I, CH_3Br, $CHBr_3$, $CHCl_3$, $CH_3{}^{13}COOH$, and CS_2, each measured over a wide range of temperatures at 15.1 MHz. Data are also given on the magnetic field dependence of $T_1(^{13}C)$ in CH_3OH, CH_3I, and $CH_3{}^{13}COOH$. The T_1 results, together with nuclear Overhauser enhancements measured for the foregoing hydrogen-containing molecules, as well as for $CH_3{}^{13}COCH_3$, $^{13}CH_3COOCD_3$, and $(CH_3)_4Si$, are interpreted in terms of the probable relaxation mechanisms.

The rapidly increasing use of ^{13}C nmr has generated considerable interest in the mechanisms by which ^{13}C nuclei relax. A knowledge of relaxation rates and the basic mechanisms that determine those rates is essential for the efficient application of Fourier transform[2a] and nuclear Overhauser enhancement (NOE) techniques.[2b]

Until the last year few data had been reported for ^{13}C relaxation times, and little interpretation had been attempted. McConnell and Holm[3] speculated on a possible relaxation mechanism for ^{13}C in CS_2; Ettinger[4] and Hunter and Reeves[5] each reported values for T_1 (^{13}C) in a few compounds; and Kuhlmann and Grant[6] interpreted NOE data for formic acid in terms of a dipolar relaxation mechanism for the ^{13}C. Olivson, Lippmaa, and Past[7] reported T_1's for ^{13}C in a number of compounds, but later results cast considerable doubt on several of their values.

Recent studies have considerably extended our knowledge of ^{13}C relaxation rates and mechanisms for some compounds. Jones[8] reported T_1's for a number of compounds at room temperature. Spiess, *et al.*,[9] made a detailed temperature and field dependence study of T_1 in CS_2, and Gillen, Schwartz, and Noggle[10] investigated CH_3I in detail. Grant and coworkers[2,11,12] used

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T_1 and NOE measurements to elucidate some aspects of relaxation mechanisms in several molecules, while Freeman and Hill[13] and Doddrell and Allerhand[14,15] used Fourier transform methods to find T_1's for individual carbon nuclei. Most recently Jaeckle, Haeberlen, and Schweitzer[16] reported and analyzed T_1 data for ^1H and ^{13}C in several molecules.[16a]

We report here measurements of $T_1(^{13}C)$ as a function of temperature for neat liquid samples of ^{13}C-enriched $CHCl_3$, $CH_3{}^{13}COOH$, CH_3OH, CH_3I, CH_3Br, $CHBr_3$, and CS_2. In addition, we have measured nuclear Overhauser enhancements for these molecules and for $CH_3{}^{13}COCH_3$, $^{13}CH_3COOCD_3$, and $(CH_3)_4Si$ at 30° and the frequency dependence of T_1 for CH_3OH, CH_3I, and $CH_3{}^{13}COOH$.

Experimental Section

All experiments except the frequency dependence studies were carried out at 15.1 MHz with a single coil pulse spectrometer fabricated at the National Bureau of Standards. For T_1 measurements 180°, τ, 90° pulse sequences were used, and the values of T_1 were obtained from least-squares fits of the logarithm of the heights of the 90° pulse responses as a function of τ. An external ^{19}F field/frequency lock was employed, and in some cases data from four runs were averaged with a Fabritek 1074 time averaging computer to improve signal/noise. The 90° pulse width was ~3 μsec, and the homogeneity of H_1 was quite good, as indicated by comparison of 90 and 270° pulse responses. The homogeneity of H_0 was adjusted to give $T_2^* \geqslant 100$ msec. Sample temperature was controlled by preheated or precooled nitrogen and was measured by a calibrated thermocouple in the effluent gas stream. Temperature accuracy is estimated as ±0.5°.

Measurements of T_1 at 9 and 19 MHz were made with an unlocked pulse spectrometer using 180°, τ, 90° sequences. Data were obtained only at room temperature, 24°.

Nuclear Overhauser enhancements (η) were measured at 15.1 MHz by noting the increase in peak-to-peak amplitude of the response to a 90° pulse when ^1H noise modulation was applied at or near proton resonance. Measurements were made near $t = 0$ with the magnetic field a few kilohertz ($\Delta\nu \gg J$) off resonance to ensure that amplitude modulation from scalar coupling would not affect the measured intensity of the undecoupled decay envelope. This method is satisfactory for the present purpose, but Fourier transformation and integration of the resulting spectral lines is required for obtaining NOE's for individual lines in more complex molecules.[15]

The temperature under decoupling conditions was kept as near room temperature as possible by blowing cold air over the decoupling coil. The temperature (30 ± 1°) was measured by inserting a thermocouple into an open sample tube with 1 cc of methanol.

Samples were thoroughly degassed by trap to trap distillation and several freeze-pump-thaw cycles. Sample tubes were 10 mm o.d., constricted to about 1 mm i.d. below the liquid surface and near the top of the rf coil in order to minimize liquid-vapor interchange. (Failure to take such precautions can affect the measured T_1 and η values due to contributions from rapidly relaxing nuclei in the vapor phase[17] as we show later.)

Samples were neat liquids of approximately 60% enriched material, obtained commercially. Because of the limited amounts of material available we were unable to carry out any purification except distillation *in vacuo* as part of the degassing procedure. Vapor phase chromatography, ir, and ^1H nmr data showed no impurities.

Results and Discussion

Relaxation Mechanisms. Several interactions can contribute to the relaxation rate, R_1 ($R_1 \equiv 1/T_1$), of a ^{13}C nucleus: (1) dipole-dipole, R_1^{d}; (2) chemical shift anisotropy, R_1^{csa}; (3) scalar relaxation, R_1^{sc}; and (4) spin-rotation, R_1^{sr}. The observed rate is the sum of these four terms.

Dipolar relaxation arises primarily from nearby nuclei with large magnetic moments, usually ^1H in the molecules studied here. (We neglect *inter*molecular dipole-dipole interactions which should be quite small.) In the "extreme narrowing condition" that characterizes the motion of small molecules, R_1^{d} for ^{13}C relaxed by ^1H is given by[18]

$$R_1^{d} = (\gamma_C{}^2\gamma_H{}^2\hbar^2/r^6)\tau_c \qquad (1)$$

where γ_C and γ_H are the magnetogyric ratios of ^{13}C and ^1H, which are separated by a distance r, and τ_c is the correlation time for the rotational motion of the internuclear vector r. τ_c varies exponentially with temperature as

$$\tau_c = \tau_c{}^0 e^{E/kT} \qquad (2)$$

As τ_c decreases with increasing temperature, R_1 also decreases.

R_1^{csa} also is proportional to the molecular reorientation time. R_1^{csa}, however, is also dependent on magnetic field[18]

$$R_1^{csa} = (2/15)\gamma_C{}^2H_0{}^2(\sigma_\parallel - \sigma_\perp)^2\tau_c \qquad (3)$$

where H_0 is the applied magnetic field, and $(\sigma_\parallel - \sigma_\perp)$ is the anisotropy in the chemical shift.[19]

R_1^{sc} arises from scalar spin coupling between ^{13}C and a nucleus that relaxes rapidly, usually by quadrupolar interactions. R_1^{sc} is given by[18]

$$R_1^{sc} = \frac{8\pi^2J^2}{3}S(S+1)\frac{T_{1S}}{1 + 4\pi^2(\nu_C - \nu_S)^2(T_{1S})^2} \qquad (4)$$

where J is the spin-spin coupling constant between ^{13}C and a spin S with relaxation time T_{1S}, and Larmor frequency ν_S. ν_C is the Larmor frequency of ^{13}C. Of the molecules studied here, only those containing I or Br are possible candidates for scalar relaxation, since these are the only nuclei where $T_{1S} \approx 1/2\pi(\nu_C - \nu_S)$. The behavior of R_1^{sc} with temperature depends on the relative magnitudes of $(\nu_C - \nu_S)$ and T_{1S}. The contribution to R_1^{sc} from ^{79}Br will increase with temperature, opposite to that from ^{81}Br and I.

R_1^{sr} depends on the interaction of ^{13}C with the overall molecular rotation[20] and is given by

$$R_1^{sr} = (2\pi IkT/h^2)C_{eff}{}^2\tau_J \qquad (5)$$

where I is the molecular moment of inertia, C_{eff} is the effective spin-rotation coupling tensor, and the correlation time τ_J is given by

$$\tau_J = I/6kT\tau_c \qquad (6)$$

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Table I. ^{13}C Spin–Lattice Relaxation Times (T_1) and Nuclear Overhauser Enhancement (η) at 30° and 15 MHz

Molecule[a]	η[b]	T_1, sec	R_1, sec^{-1}	R_1^d, sec^{-1}	R_1^{other}, sec^{-1}	Ref
$CHCl_3$	1.75	32.4 ± 0.5	0.0309	0.027	0.004	
$CH_3{}^{13}COOH$	1.44	41.1 ± 0.6	0.0243	0.018	0.006	
CH_3OH	0.92	17.5 ± 0.3	0.057	0.027	0.031	
	0.73	13.4 ± 0.8	0.075	0.027	0.048	11
CH_3I	0.52	13.4 ± 0.2	0.075	0.019	0.056	
	0.42	11.1 ± 0.4	0.090	0.019	0.071	11
		14.2 ± 0.4	0.070			10
CH_3Br	0.30	8.8 ± 0.2	0.114	0.017	0.097	
$CHBr_3$	0.30	1.65 ± 0.05	0.61	0.10	0.51	
$CH_3{}^{13}COCH_3$	0.19	36.1 ± 0.3	0.0277	0.003	0.025	
$^{13}CH_3COOCD_3$	1.00	19.2 ± 0.4	0.0520	0.026	0.026	
$(CH_3)_4Si$	1.65					

[a] ^{13}C enrichment about 60%, except $(CH_3)_4Si$, which is 5% enriched. [b] The estimated accuracy of $1 + \eta$, the intensity ratio, is ±10%.

Thus R_1^{sr} varies inversely with τ_c, hence *increases* with increasing temperature.

Studies of the temperature dependence of T_1 can, then, provide insight into the contributions from the various relaxation mechanisms. In addition, a direct measure of the contribution from dipole–dipole interaction with nearby protons may be obtained from the results of nuclear Overhauser enhancement studies. Kuhlmann, *et al.*,[2] showed that η, the fractional increase in the intensity of the ^{13}C signal on irradiation at the proton resonance frequency, is given by

$$\eta = 1.988(R_1^d/R_1) \qquad (7)$$

Thus from a measurement of R_1 and of η, R_1^d can be calculated.

T_1 and NOE Data. Table I summarizes our NOE results, together with values of R_1 and R_1^d, for the hydrogen-containing molecules at 30°. Three of these molecules have also been examined by Lyerla, *et al.*,[11] using the same method. (For CH_3COOH, however, their results refer to the CH_3 carbon.) Their data were obtained with cw, rather than pulse methods, with R_1's determined by adiabatic rapid passage. As indicated in Table I, their data and ours for CH_3OH and CH_3I are in substantial agreement, although small discrepancies exist which will be discussed below.

Figure 1 shows the temperature dependence of R_1 at 15.1 MHz for six of these molecules and CS_2. The straight lines with positive slope obtained for $CHCl_3$ and $CH_3{}^{13}COOH$ indicate that R_1 is mostly dipolar, in agreement with the NOE values (η = 1.75 and 1.44) obtained at 30°.

The curve for CH_3OH shows that R_1^d dominates over most of the temperature range with increasing contributions from R_1^{sr} at higher temperatures. The curve was resolved into two straight lines with opposite slope, from which the contributions from spin-rotation and dipole–dipole relaxation were estimated.[21] At 30° this graphic analysis yielded $R_1^{sr} = 0.024$ sec^{-1} and $R_1^d = 0.033$ sec^{-1}, in agreement within experimental error with the values $R_1^{other} = 0.031$ sec^{-1} and $R_1^d = 0.027$ sec^{-1} obtained from the NOE measurement. The value obtained for R_1^d in this study agrees well with that found by Lyerla, *et al.*[11] ($R_1^d = 0.027$ at ~35°), while their value for R_1^{other} (0.048 sec^{-1}) is substantially higher than ours. This discrepancy is outside the range of experimental errors in T_1 determinations, and the higher value obtained by Lyerla, *et al.*,[11] may be due to additional spin–rotation relaxation from molecules in the vapor phase (see below).

The R_1 values for CH_3I were observed to be almost independent of temperature and in agreement with those obtained by Gillen, *et al.*[10] The measurement of the NOE at 30°, η = 0.49, shows that the dipolar contribution is small ($R_1^d = 0.019$ sec^{-1}; while $R_1^{other} = 0.056$ sec^{-1}), and the relaxation at this temperature is evidently dominated by spin-rotation.

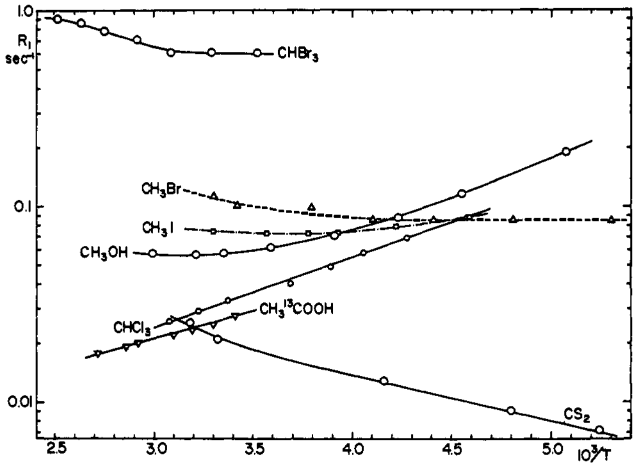

Figure 1. ^{13}C relaxation rates as a function of inverse absolute temperature at 15.1 MHz.

Room temperature (24°) measurements at 9.2 and 19 MHz gave the same value (13.5 sec) for T_1 as at 15.1 MHz. The S/N of these measurements was considerably poorer, and we conservatively estimate the error limits as ±2 sec. Gillen, *et al.*,[10] speculated on the possible importance of scalar coupling as a relaxation mechanism for ^{13}C in CH_3I. The present measurements indicate that scalar coupling is at best of very minor importance for ^{13}C bound directly to ^{127}I.[22]

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(21) From the graphic analysis an activation energy $E_a^d = 1.95 \pm 0.05$ kcal/mol was obtained for R_1^d, and an exponential factor $E_a^{sr} = -2.2 \pm 0.2$ kcal/mol for R_1^{sr}. E_a^d is only slightly higher than that observed for methyl iodide[10] (1.43 kcal/mol), whereas E_a^{sr} is considerably larger in magnitude than the value (−0.7 kcal/mol) obtained for CH_3I.[10] Even considering the limitations in the accuracy of resolving the curve, it seems that the hydrogen bonding in methanol may have profound effect on the spin–rotation contribution.

(22) The maximum error limit of ±2 sec for ^{13}C T_1 obtained at 9.2 MHz allows an upper limit to be estimated for J_{CI} from eq 4. Using the ^{127}I relaxation time 2.5×10^{-7} sec calculated by Gillen, *et al.*,[10] we obtain $R_1^{sc} = 2.3 \times 10^{-6} \times J_{CI}^2$ at 15.1 MHz and $R_1^{sc} = 5.9 \times 10^{-6} \times J_{CI}^2$ at 9.2 MHz. Assuming negligible contribution from chemical shift anisotropy, we can combine the lowest possible value for T_1 at 9.2 MHz (11.5 sec) with T_1 = 13.4 sec at 15.1 MHz to obtain an upper limit for J_{CI} of ~60 Hz.

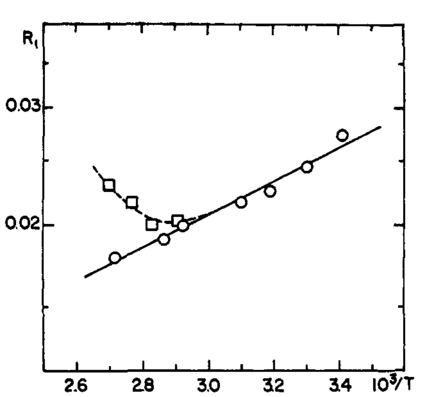

Figure 2. ^{13}C relaxation rates for $CH_3{}^{13}COOH$ as a function of inverse absolute temperature at 15.1 MHz: solid line, sample tube geometry as described in text; dashed line, conventional sample tube.

The temperature dependence of R_1 for CH_3Br is qualitatively similar to that of CH_3I, suggesting presence of spin-rotation and dipole–dipole relaxation mechanisms. The low value of the Overhauser effect ($\eta = 0.29$) gives $R_1{}^d = 0.017$ sec^{-1} out of the total relaxation rate at room temperature, 0.114 sec^{-1}. However, an additional contribution from scalar relaxation is expected since the Larmor frequency of ^{79}Br is not very different from that of ^{13}C ($\nu_C - \nu_{Br} \simeq 54$ kHz). Assuming that the correlation time τ_c is similar to that for CH_3I ($\sim 1.4 \times 10^{-12}$) and using a quadrupole coupling constant of $\sim$550 MHz (intermediate between those measured in the solid[23] and in the gas[24]), we can calculate the ^{79}Br relaxation time $T_1^Q \simeq 6 \times 10^{-7}$ sec. From eq 4 the scalar contribution $R_1{}^{sc} \sim 6 \times 10^{-5} \times J^2$ sec can be derived. For reasonable values of J (10–50 Hz) scalar relaxation can be seen to be important. Unfortunately, field dependence studies are of no use in this case because of the small magnitude of $\nu_C - \nu_{Br}$.[25] The effect of ^{81}Br should vary with field strength, but the magnitude of the scalar contribution is much smaller and the presence of both isotopes makes such an experiment not very promising.

For $CHBr_3$, however, scalar relaxation probably is the dominant relaxation mechanism. R_1 is an order of magnitude larger than for the other molecules, and the low value of η (0.34) shows that dipole–dipole interaction is not dominant. It seems unlikely that spin rotation would contribute more in $CHBr_3$ than in $CHCl_3$, and in the latter it was shown to be negligible. Thus we conclude that scalar relaxation is the dominant relaxation mechanism for $CHBr_3$.

The temperature dependence curve for CS_2 shows that R_1 is dominated by spin rotation. Spiess, *et al.*,[9] in a careful temperature and field dependence study also concluded that spin rotation is dominant at 15 MHz, but that $R_1{}^{csa}$ contributes at low temperatures and high fields.

In addition to the measurements of R_1 for CH_3I at other frequencies R_1 for CH_3OH and $CH_3{}^{13}COOH$ was measured at 9.2 and 19.0 MHz. R_1 of CH_3OH, as expected, was found to be independent of field strength. For $CH_3{}^{13}COOH$ at 24° we found a small apparent dependence of R_1 on frequency ($R_1 = 0.0249$, 0.0261, and 0.0279 sec^{-1} at 9.2, 15.1, and 19.0 MHz, respectively). Results at higher frequencies from other laboratories[27,28] seemed to confirm this dependence, but a recent study by Haeberlen[29] at 61 MHz gave $R_1 = 0.0268$ sec^{-1} at 24.5°, indicating that $R_1{}^{csa}$ is negligible for $CH_3{}^{13}COOH$. The value obtained for η (1.44) then suggests the presence of spin-rotation interaction and/or a possible contribution from scalar relaxation if the exchange of the carboxyl proton takes place at an appropriate rate.

Included in Table I are values of η and T_1 for $CH_3{}^{13}COCH_3$ and $^{13}CH_3COOCD_3$. The low NOE's obtained for these molecules are probably ascribed to spin-rotation interaction. For $^{13}CH_3COOCD_3$ this interpretation is in qualitative agreement with the conclusion drawn by Gillen, *et al.*,[10] and Lyerla, *et al.*,[11] that (internal) spin-rotation contributes strongly to the relaxation of ^{13}C in methyl groups. The observed value of $\eta = 1.65$ for $(CH_3)_4Si$, however, indicates that steric interference between the four methyl groups restricts their internal rotation.

Effects of Sample Configuration and Oxygen. It is known that the spin-rotation contribution to relaxation in the vapor phase can be orders of magnitude larger than in the liquid.[30] If care is not taken to impede liquid–vapor interchange, the apparent R_1 for a volatile liquid may be much larger than the true value, since a large portion of the relaxation actually occurs in the vapor. Our results were obtained with tubes constricted between the measured portion of the liquid and the liquid surface.[17] This type of sample tube effectively precludes rapid relaxation in the vapor from affecting the liquid phase relaxation results. With the ordinary cylindrical sample tube configuration, erroneous large values of R_1 may be obtained in the temperature region immediately below the boiling point. This artifact is clearly demonstrated in Figure 2 for $CH_3{}^{13}COOH$. It is possible that liquid–vapor interchange in the experiments of Lyerla, *et al.*,[11] may account for the small discrepancies in the values of $R_1{}^{other}$ for CH_3OH and CH_3I.

All data reported here are for samples that were carefully degassed. We have not studied in detail the effect of dissolved oxygen, but we did make one observation for $CH_3{}^{13}COOH$, which has a rather long T_1, and hence should be sensitive to small changes. Opening the sample tube and shaking it increased R_1 from 0.025 sec^{-1} to approximately 0.05 sec^{-1}. This increment, of about 0.025 sec^{-1}, is an order of magnitude smaller than that commonly found for dissolved oxygen affecting ^{1}H relaxation, typically of the order of 0.3 sec^{-1}. Similar results were recently reported by Jaeckle, *et al.*[16]

Conclusion

On the basis of the new data presented here, together with other recently reported results, we can make the

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(24) W. Gordy, J. W. Simmons, and A. G. Smith, *Phys. Rev.*, 74, 243, 1246A (1948).

(25) In principle $R_1{}^{sc}$ in both CH_3Br and CH_3I can be found from measurements of T_2. However, the effect on T_2 of scalar relaxation from the protons[26] must be eliminated by very rapid pulsing ($^1/_2\ \tau > 10^3$ sec^{-1}), a pulse rate not attainable with our apparatus.

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following observations about ^{13}C relaxation in small molecules. 1. The relaxation is primarily due to ^{1}H–^{13}C dipole–dipole interaction if ^{13}C is bonded directly to one or more protons. 2. Spin rotation can be expected to contribute in small molecules, especially at temperatures near the boiling point, and to be a dominant relaxation mechanism for CH_3 groups due to the free internal rotation about the CH_3–R bond. 3. Chemical shift anisotropy is, in general, not a significant relaxation mechanism. 4. Scalar relaxation only rarely contributes to R_1 and then only when ^{13}C is bonded to an appropriate quadrupolar nucleus, such as ^{79}Br and ^{81}Br, but probably never ^{127}I.

Acknowledgment. We wish to thank Dr. U. Haeberlen for making available to us his data on T_1 in $CH_3{}^{13}COOH$ at 61 MHz.

Molecular Orbital Theory of the Electronic Structure of Organic Compounds. IX. A Study of n → π^* Transition Energies in Small Molecules[1a]

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Abstract: *Ab initio* minimal basis SCF–CI calculations have been performed on a series of small molecules possessing uv bands which may be attributed to n → π^* excitations. The calculated results show that this level of theory can give an adequate description of such transition energies. The changes in transition energies produced by substitution on four chromophores are analyzed in detail.

Organic molecules which contain nitrogen or oxygen in an unsaturated group often possess low-energy uv absorption bands of rather low intensity. These bands are known to be due to the excitation of nonbonding (n) electrons into antibonding π orbitals and have been called n → π^* bands by Kasha.[2] Experimental studies of such excitations have led to many correlations between transition energy and the nature and environment of the absorbing group, and there have been many theoretical attempts to explain these data. The earliest theoretical studies were all based on approximate theories which neglected electron interaction.[3] At this level, transition energies are given by the difference of the n and π^* one-electron orbital energies, and substituent effects are discussed in terms of the way in which a particular substituent raises or lowers the energies of these orbitals. Although a theory which neglects electron interaction cannot give an overall correct picture of electronic spectra, it has been useful in rationalizing trends within restricted classes of compounds. At the semiempirical level, improvements were obtained by incorporating electron interaction into the theory, but this was usually done in an approximate manner.[4]

Although there have been several *ab initio* molecular orbital studies of n → π^* excited states,[5,6] there has been no systematic study at a uniform level of approximation. The aim of this work is to present such a study of n → π^* excited singlet states for a group of small molecules containing the chromophores $>C{=}O$, $>C{=}N{-}$, $-N{=}N-$, and $-N{=}O$ and which (1) are acyclic; (2) contain only H, C, N, O, and F; (3) contain up to three heavy atoms (C, N, O, or F); and (4) may be represented in the ground state by a classical valence structure with no formal charges or unpaired electrons associated with any atom. The group of carbonyl compounds has been enlarged to include a greater variety of monosubstituted compounds and some disubstituted molecules, since these are particularly appropriate for examining substituent effects.

For this study each ground state is described by a single determinant of doubly occupied molecular orbitals, ψ_i, each of which is constructed from a minimal basis of Gaussian-fitted Slater-type atomic orbitals ϕ_μ. Wave functions, Ψ_i^l, describing singly excited configurations are formed from the ground-state wave function by promoting electrons from doubly occupied orbitals ψ_i to virtual orbitals ψ_l. Some allowance for electron reorganization on excitation is then made by permitting mixing of configurations representing different singly excited virtual states.

Quantum Mechanical Method

The quantum mechanical method used is that given in detail in ref 7. The closed-shell ground-state Ψ is rep-

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[3] See J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, New York, N. Y., 1961; or A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

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