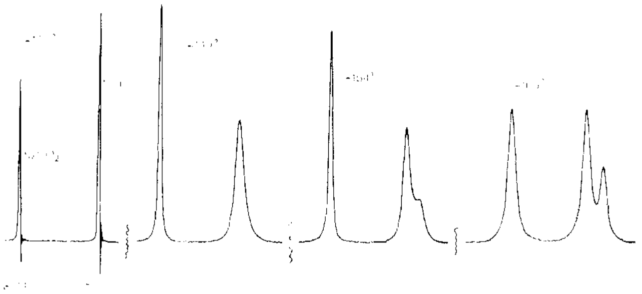
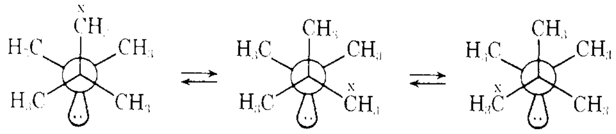


Figure 1. The pmr spectrum (60 MHz) of *tert*-butyldimethylamine (10% by volume in CH_2CHCl) as a function of temperature.

metry[3] and rotation is the only rate process which would be expected to affect the nmr spectrum.

Examination of the pmr spectrum (60 MHz) of I (15% by volume in CH_2CHCl) at −100° revealed two sharp singlet resonances due to the *tert*-butyl (δ 1.00) and methyl (δ 2.14) groups (Figure 1). Upon lowering the temperature, the *tert*-butyl resonance (δ 1.00) broadens and separates into two overlapping peaks with an area ratio of 1:2 (Figure 1). The shape of the $N(CH_3)_2$ peak (δ 2.14, Figure 1) is essentially independent of temperature except for some broadening due most likely to viscosity effects and ^{14}N quadrupole relaxation.

Since slowing of the nitrogen inversion process does not generate a center of asymmetry in I as it does in dibenzylmethylamine,[3] slow inversion cannot account for the spectral transitions described in Figure 1. The most plausible rationalization is a slowing of rotation about the *tert*-butyl–nitrogen bond. Perusal of eq 1 indicates that in any of the three equivalent rotamers (Newman projection looking down the central *tert*-butyl carbon–nitrogen bond), the *N*-methyls always experience equivalent environments and should display an nmr spectrum independent of any rate process save CH_3–N rotation. However, for the *tert*-butyl group in any given rotamer (eq 1), there are two equivalent methyls bisected by the nitrogen lone pair and one other different methyl which bisects the $N(CH_3)_2$ group. In the event of slow rotation of *tert*-butyl (eq 1), the *tert*-butyl resonance should consist of two singlets of relative intensity 1:2 as observed (Figure 1). It is also clear from eq 1 that the three methyls of the *tert*-butyl group do indeed exchange environments *via* rotation and that rapid rotation on the nmr time scale will result in a singlet resonance.



(1)

Total line-shape analyses[4] for the *tert*-butyl resonance over the temperature range from −161 to −137° have been performed. It is clear from the nmr spectra (Figure 1) that the width at half-height ($W_{1/2}$) of the $N(CH_3)_2$ resonance (δ 2.14) increases as the temperature is lowered, especially from *ca.* −110 to −166°. This is due to a lowering of the spin–spin relaxation time (T_2) due to viscosity and ^{14}N quadrupole relaxation. However, examination of the nmr spectrum of I at −80° (fast exchange conditions) shows that $W_{1/2}$ for the $N(CH_3)_2$ resonance is equal to $W_{1/2}$ for the *tert*-butyl peak. In addition, perusal of the nmr spectrum of I at −166° (Figure 1) reveals equal intensities for the larger of the two *tert*-butyl resonances and the $N(CH_3)_2$ peak. Since these peaks should have an area ratio of 1:1, the data strongly imply equal widths at half-height. Indeed, the best "fit" of theoretical to experimental spectra for the *tert*-butyl resonances at −166° was obtained using $W_{1/2}$ equal to that of the $N(CH_3)_2$ peak. In all subsequent line-shape calculations at different temperatures it was assumed therefore that the $N(CH_3)_2$ $W_{1/2}$ accurately reflected the C–CH_3 $W_{1/2}$. In addition, it is observed that the chemical shift of the *tert*-butyl resonance under conditions of fast exchange (*e.g.*, −80°) is predicted accurately using the properly weighted chemical shifts of the two *tert*-butyl peaks observed at −166°, *i.e.*, the chemical shifts of the *tert*-butyl resonances are essentially independent of temperature. A series of rate constants (k = first-order rate constant for the disappearance of any methyl of the *tert*-butyl group from any one of the three sites; eq 1) as a function of temperature was obtained by matching calculated[4] to experimental nmr spectra. A least-squares treatment of ln k *vs.* $1/T$ (correlation coefficient = 0.998) gave $E_a = 6.4 \pm 0.2$ kcal/mol, $\Delta H^{\ddagger} = 6.2 \pm 0.2$ kcal/mol, $\Delta G^{\ddagger} = 6.0 \pm 0.1$ kcal/mol at −153°, and $\Delta S^{\ddagger} = 1.3 \pm 1.5$ eu.

The above results indicate clearly that barriers to rotation about C–N single bonds can be determined by variable-temperature nmr spectroscopy and that total nmr line-shape analysis will give all the activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta G^{\ddagger}$, E_a) for such a process. It is also clear that the barriers to inversion and rotation in simple acyclic trialkylamines are similar and that either process may be detected depending on the structure of the amine.[3]

We are investigating steric effects on the rotational barriers in simple amines and these results will be reported in due course.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. GP 18197) and Research Corporation for support as well as the Worcester Area College Computation Center for donated computer time.

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(3) M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, 339 (1970); C. H. Bushweller and J. W. O'Neil, *J. Amer. Chem. Soc.*, 92, 2159 (1970).

(4) C. H. Bushweller, J. Golini, G. U. Rao, and J. W. O'Neil, *ibid.*, 92, 3055 (1970). See ref 5 in the above paper.

(5) Supported by a NASA Traineeship, 1969–1970.

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Copper(II) Propionate-*p*-Toluidine. A Cupric Carboxylate Adduct of Novel Polymeric Structure

Sir:

Many studies of copper(II) carboxylates have been stimulated by interest in the nature of the metal–metal interaction exhibited by some of these compounds.[1-5]

(1) M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 64, 99 (1964).

For complexes of stoichiometry $Cu(O_2CR)_2L$, a dimeric structure is commonly assumed if the room-temperature magnetic moment is less than 1.9 BM and if the variation of the observed magnetic susceptibility with temperature agrees with that calculated for a magnetically isolated pair of interacting spins.[6,7] Such studies on copper(II) *n*-alkanoate adducts having a wide variety of alkyl substituents R and addends L have been reported. For the complexes considered to be dimers, $[Cu(O_2CR)_2L]_2$, the magnetic properties appear to be relatively insensitive to the nature of the alkyl group or of the donor ligand ($-2J$ = 250–330 cm^{-1}, μ_{eff} = 1.3–1.5 BM).[8] However, the magnetic data for the adducts of copper(II) *n*-alkanoates with aniline and its derivatives suggest that these particular compounds are exceptional ($-2J = 112 \pm 12$ cm^{-1}, $\mu_{\text{eff}} = 1.75 \pm 0.02$ BM).[9] Our interest in this anomaly led us to investigate the structure of a *p*-toluidine adduct of copper(II) propionate.

Adducts of cupric *n*-alkanoates with aniline derivatives are unstable, particularly in solution. However long plate-like, dark green crystals of the *p*-toluidine adduct of copper(II) propionate have been obtained under anhydrous conditions. The compound was recrystallized at −5° from spectroscopic grade acetone containing a slight excess of *p*-toluidine. The compound has an effective magnetic moment at 295°K of 1.4 BM. Its visible absorption spectrum in benzene shows peaks at 3850 and 6900 Å whose intensity ratio is concentration dependent.[10] The former peak has a much greater intensity than those reported by Kokot and Martin[9] for any butyrate adduct at equivalent concentrations in benzene. This together with the different magnetic moment of the present compound indicate that it may well be structurally dissimilar from their acetate and butyrate aniline adducts. The crystals have triclinic symmetry with reduced unit cell parameters a = 12.466 (7), b = 12.183 (6), c = 11.598 (6) Å, α = 116° 2′ (2′), β = 91° 44′ (2′), γ = 73° 49′ (2′). Calculated (Z = 4) and observed densities are 1.39 and 1.36 (2) g/cm^3, respectively. The structural analysis was based upon 1191 independent nonzero reflections, collected by the θ–2θ scan technique with Cu Kα radiation on a Picker diffractometer. An absorption correction was applied to the observed intensities.

The structure was successfully solved in space group $P\bar{1}$ by the usual Patterson and Fourier methods. Full-matrix isotropic least-squares refinement, with the rings of the *p*-toluidine ligands treated as rigid groups and anisotropic thermal parameters assigned to the copper atoms, has converged to a conventional R factor of 0.082. Evidence exists for some disorder involving the ethyl groups. This difficulty should not significantly affect the parameters of the copper atoms and their inner coordination spheres reported here.

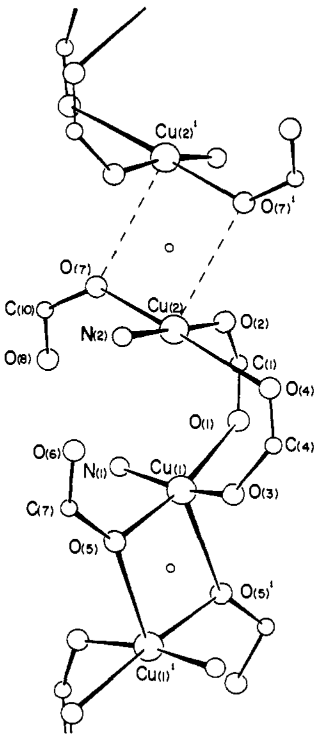

Figure 1. A view of a portion of the one-dimensional polymeric structure of $Cu(O_2CC_2H_5)_2$–p-$CH_3C_6H_4NH_2$. Ethyl and *p*-tolyl groups have been omitted for clarity. Primes refer to atoms related to those in the asymmetric unit by a crystallographic center of symmetry. Bond lengths about the copper ions not mentioned in the text include: Cu(1)–O(1) = 1.92 (1), Cu(1)–O(3) = 1.92 (1), Cu(1)–N(1) = 2.04 (1), Cu(2)–O(2) = 1.96 (1), Cu(2)–O(4) = 1.92 (1), Cu(2)–O(7) = 1.89 (1), and Cu(2)–N(2) = 2.07 (2) Å.

The structure of $Cu(O_2CC_2H_5)_2$–p-$CH_3C_6H_4NH_2$ (with ethyl and *p*-tolyl groups omitted for clarity) is shown in Figure 1. The complex is not a dimer in the solid state, but rather may be regarded as a one-dimensional polymer with the metal–metal vectors forming a zigzag chain along the a direction. Both crystallographically independent copper atoms may be considered to have a distorted square-pyramidal configuration with one *p*-toluidine nitrogen atom and three carboxylate oxygens in the basal plane with the metal atom. In each case, two adjacent basal oxygen atoms are associated with a bidentate carboxylate group of syn,syn configuration[11] bridging the two independent coppers. The third basal oxygen atom at each metal atom forms a monatomic bridge to the apex of an adjacent square pyramid. This latter type of bridging function for a carboxylate group has not previously been reported.[12]

Three distinct types of copper–copper linkage exist. (a) Cu(1) and Cu(2) are joined by two triatomic carboxylate bridges. This portion of the structure is reminiscent of the dimeric copper(II) carboxylate structures. The Cu(1)–Cu(2) distance is 3.197 (4) Å. (b) Cu(1) and Cu(1)′ are linked through two monatomic

(2) C. Oldham, *Progr. Inorg. Chem.*, 10, 223 (1968).

(3) R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., University Press, Cambridge, England, 1968, pp 175–231.

(4) W. E. Hatfield and R. Whyman, *Transition Metal Chem.*, **5**, 47 (1969).

(5) G. F. Kokoszka and G. Gordon, *ibid.*, **5**, 181 (1969).

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(7) R. W. Jotham and S. F. A. Kettle, *J. Chem. Soc. A*, 2816, 2821 (1969); *Inorg. Chem.*, **9**, 1390 (1970).

(8) $-2J$ is an estimate of the energy separation between the singlet and triplet levels arising from pairwise magnetic interaction between metal atoms.

(9) E. Kokot and R. L. Martin, *Inorg. Chem.*, **3**, 1306 (1964).

(10) The product gives acceptable Cu, C, H, and N analyses for $CuC_{13}H_{19}O_4N$. Its visible spectrum obtained on a Cary 14 in C_6H_6 shows: 0.005 M, 3850 Å, ϵ 289; 6900 Å, ϵ 136; 0.002 M, 3500–4300 (sh), ϵ ~120; 6900 Å, ϵ 105.

(11) Nomenclature of various metal bridging carboxylate configurations has been discussed by R. L. Martin and H. Waterman, *J. Chem. Soc.*, 1359 (1959).

(12) S. Herzog and W. Kalies, *Z. Chem.*, **8**, 81 (1968).

bridges. The Cu(1)–O(5) and Cu(1)–O(5)′ bond distances within this arrangement are 1.95 (1) and 2.31 (1) Å, respectively. The resulting metal–metal separation is 3.271 (6) Å. (c) The Cu(2)–Cu(2)′ linkage is similar to that between Cu(1) and Cu(1)′, but with a considerably longer copper–apical oxygen bond (Cu(2)–O(7)′ = 2.46 (1) Å) and a copper–copper distance of 3.341 (6) Å. Interactions b and c join square-pyramidal copper polyhedra along common apical edges. In view of the long Cu(2)–O(7)′ distance, the linear polymer might also be regarded as comprised of tetrameric units.

Because of the long metal–metal distances and of the low symmetry of the individual metal pairs in this complex, any magnetic interaction would most probably arise through a superexchange mechanism. Spin coupling could, in principle, occur within any of the three types of copper–copper pairs, within an infinite one-dimensional lattice or in some combination of interactions. Further investigations of these points and of the relationship of the compound to the aniline adducts prepared by Kokot and Martin[9] are in progress.

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The Mechanism of Photochemical Addition of *trans*-Stilbene to Tetramethylethylene[1]

Sir:

Photoaddition of *trans*-stilbene to tetramethylethylene gives *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane in high yield.[2] The quantum yield for adduct formation (Φ_a) is 0.54 at 313 nm with 4 M tetramethylethylene (TME) in hexane. The quantum yield is constant to at least 20% conversion. Conversions were kept to 5% or less in the experiments reported. A plot of $1/\Phi_a$ *vs.* 1/[TME] is linear (Figure 1, intercept 1.0, slope 4.2) in accord with expectation for a process in which electronically excited *trans*-stilbene adds to ground-state tetramethylethylene. The quantum yield (4 M olefin) is temperature dependent and increases by a factor of almost three as the temperature is lowered from 65 ($\Phi = 0.24$) to 5° ($\Phi = 0.69$).[3] The addition is not sensitized by sensitizers (thioxanthone, Michler's ketone) which sensitize the trans to cis isomerization of *trans*-stilbene. This result suggests that the addition involves singlet-excited *trans*-stilbene. Direct evidence that the addition involves the low lying singlet excited state (S_1) of *trans*-stilbene is provided by tetramethylethylene quenching of *trans*-stilbene fluorescence. A plot of the ratio of the quantum efficiency of fluorescence in the absence of olefin to that in the presence of olefin, $\Phi_f/(\Phi_f)_{\text{olefin}}$, *vs.* tetramethylethylene concentration is linear (slope 0.20, intercept 1.0, Figure 2).

If one considers the simplest possible mechanism for photochemical cycloaddition of *trans*-stilbene (S_t) to tetramethylethylene (O), it is possible to derive an

$$S_t + h\nu \longrightarrow {}^1S_t$$

$${}^1S_t \xrightarrow{k_d} S_t$$

$${}^1S_t \xrightarrow{k_f} S_t + h\nu_f$$

$${}^1S_t \xrightarrow{k_{ic}} {}^3S_t$$

$${}^1S_t \xrightarrow{k_c} S_c \text{ (trans} \longrightarrow \text{cis isomerization)}^5$$

$${}^1S_t + O \xrightarrow{k_{add}} \text{adduct}$$

expression for $1/\Phi_a$ as a function of olefin concentration $[\tau = 1/(k_d + k_{ic} + k_c + k_f)]$. It should be possible

$$\frac{1}{\Phi_a} = \frac{1}{\tau k_{add}[O]} + 1$$

then to determine k_{add} from the slope of the $1/\Phi_a$ *vs.* 1/[O] plot since the lifetime (τ) of the low lying singlet excited state of stilbene is known. The rate constant (k_{add}) so determined is not a true rate constant for it shows a negative temperature dependence (Figure 3). It is clear that a more sophisticated mechanism is required. The negative temperature dependence of the observed rate constant (k_{add}) suggests the presence of a prior equilibrium.

The efficient, endothermic quenching of the S_1 state of *trans*-stilbene by tetramethylethylene suggests that an exciplex is formed.[8,9] If exciplex formation is reversible, the negative temperature dependence of the observed rate constant and the other known facts are consistent with the mechanism shown below. Expressions can be derived for $1/\Phi_a$ as a function of 1/[O]

$$S_t + h\nu \longrightarrow {}^1S_t$$

$${}^1S_t \xrightarrow{k_d} S_t$$

$${}^1S_t \xrightarrow{k_f} S_t + h\nu_f$$

$${}^1S_t \xrightarrow{k_{ic}} {}^3S_t$$

$${}^1S_t \xrightarrow{k_c} S_c$$

$${}^1S_t + O \underset{k_{-e}}{\overset{k_e}{\rightleftarrows}} \text{exciplex } [{}^1S_t \cdots O]$$

$$\text{exciplex} \xrightarrow{k_a} \text{adduct}$$

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[1] Photochemical Transformations. XXXIX.

[2] O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, 90, 2333 (1968).

[3] The increased efficiency of cycloadditions at low temperature has been reported by de Mayo, *et al.*[4]

[4] R. O. Loutfy, P. de Mayo, and M. R. Tchir, *J. Amer. Chem. Soc.*, 91, 3984 (1969).

(5) Saltiel[6] has argued that isomerization of *trans*-stilbene involves isomerization of singlet-excited stilbene while Fischer[7] maintains that the isomerization involves triplet-excited stilbene. The singlet isomerization step is included in our mechanism to cover all possibilities. Our arguments would not change if $k_c = 0$.

(6) J. Saltiel, *J. Amer. Chem. Soc.*, 90, 6394 (1968); J. Saltiel, E. D. Megarity, and K. G. Kneipp, *ibid.*, **88**, 2336 (1966).

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(8) S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, 90, 2957 (1968).

(9) Singlet exciplexes are widely accepted while triplet exciplexes are still a matter of debate.[10]

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