Figure 1. Measured rate constants $k_{r,n}$ (●) for intramolecular hydrogen abstraction in **3** and fraction of reactive conformations (O), both plotted against chain length. The latter quantities are obtained from lattice-based Monte Carlo calculations (ref 11). The reactive sites are taken to be the two lattice sites adjacent to the ketone oxygen in **3** coplanar with the rings. These represent the space occupied by the nonbonding orbitals on this oxygen in **1**. Error bars represent one standard deviation.

about the ketone oxygen in **3**. Since the methyl group is unreactive in **3**,[3f] one sums over $n - 1$ carbons only.

To demonstrate that the hydrocarbon chains in **1** are randomly oriented and flexible within the stricture of tetrahedral bond angles, one must calculate $\Sigma P_{i,n}$ as a function of n for such a flexible chain. We have presented[11] a lattice-based Monte Carlo method for estimating hydrocarbon chain conformations in molecules such as **1**. This method takes rigorous account of the volume excluded by the chain and the benzophenone. By choosing certain lattice sites as reactive (e.g., those adjacent to the reactive C=O in **3**), one may estimate the total number of reactive conformations, $m_{r,n}$, for a chain n carbons long. One can also estimate the total number of conformations, $m_{t,n}$, available on a diamond lattice to a chain of length n. The ratio of (reactive conformations/all conformations) for an n carbon chain equals $\Sigma P_{i,n}$ for a flexible hydrocarbon chain.

$$\sum_{i}^{n-1} P_{i,n} = \frac{m_{r,n}}{m_{t,n}} \qquad (3)$$

While the details of the calculations, and of modeling molecules like **1** in a tetrahedral lattice, have been presented before,[11] it is important that we emphasize certain weaknesses and artifacts inherent in these calculations. Lattice-based calculations assume equal bond lengths for C–O, C–C, and C–H; consequently, C–H bond lengths are exaggerated. Hard sphere potentials underestimate CH–HC nonbonding interactions and seem to exaggerate steric interactions of CH_2 groups with the faces of the aromatic rings. The first two tend to off-set one another. The net effect, however, is to exaggerate somewhat the length of the shortest chain which can achieve a reactive conformation. This artifact has been described in some detail.[12] A more troublesome detail is that we are unable in these calculations to distinguish gauche from trans

rotamers in the chain. This has the effect of biasing the $(m_{r,n}/m_{t,n})$ ratios we calculate in favor of more highly coiled conformations of the chain. The extent to which this perturbs the calculated curve in Figure 1 is unknown.

Figure 1 presents both the experimentally determined dependence of $k_{r,n}$ on chain length and the ratio of (reactive conformations/all conformations) estimated from the Monte Carlo calculations. The horizontal shift between the two curves is consistent with the limitations of the lattice model discussed above. Choosing the reactive distance at twice the O–H bond length in **4** shifts the calculated curve so that 11 carbon chains become reactive. Expanding the reactive volume has no effect on the curve shape.

The agreement between the experimental results and the calculated reactive fraction of chain conformations for a randomly oriented flexible chain is excellent. The agreement is at the limit of what one might expect for the theoretical model at its current level of sophistication.

While rigorous conclusions cannot be drawn until quantitative calculations show that our data are inconsistent with alternative models, it seems unlikely that hairpin conformations[2c,d] or micellar aggregation with extended chains[2a,b] are favored in dilute carbon tetrachloride solution. It is possible that a small, unfavorable solvent-chain enthalpy acts to cause gauche and trans rotamers in the chain to become isoenergetic. The chains, however, appear to be highly flexible; within the framework of tetrahedral bond angles, they assume all possible orientations.

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Received June 6, 1974

Effect of Crown Ether on the Conformational Equilibrium of Sodium Acetylacetonate

Sir:

The structures of enolate anions derived from β-dicarbonyl compounds have long been a topic of interest.[1-11] Dynamic nuclear magnetic resonance

(11) M. A. Winnik, R. E. Trueman, G. Jackowski, D. S. Saunders, and S. G. Whittington, *J. Amer. Chem. Soc.*, **96**, 4843 (1974).
(12) M. A. Winnik, D. S. Saunders, G. Jackowski, and R. E. Trueman, *J. Amer. Chem. Soc.*, submitted for publication.

(1) E. E. Ernstbrunner, *J. Chem. Soc. A*, 1558 (1970).
(2) A. J. Carty, D. G. Tuck, and E. Bullock, *Can. J. Chem.*, **43**, 2559 (1965).
(3) K. Shobatake and K. Nakamoto, *J. Chem. Phys.*, **49**, 4792 (1968).
(4) H. E. Zaugg and A. D. Schaefer, *J. Amer. Chem. Soc.*, **87**, 1857 (1965).
(5) W. O. George and V. G. Mansell, *Spectrochim. Acta, Part A*, **24**, 145 (1968).
(6) N. Bacon, W. O. George and B. H. Stringer, *Chem. Ind. (London)*, 1377 (1965).
(7) O. Siiman, J. Fresco, and H. B. Gray, *J. Amer. Chem. Soc.*, **96**, 2347 (1974).
(8) R. L. Lintvedt and H. F. Holtzclaw, Jr., *Inorg. Chem.*, **5**, 239 (1966).

spectroscopy has been shown to be a powerful tool for conformational studies of related 6π-electron systems,[12-14] and we now report its application to a study of sodium acetylacetonate. We have been able to measure the barrier to conformational interchange in a β-diketone enolate anion, and to make reliable configurational assignments. In addition, our results show that cation–anion interactions are of sufficient energy to reverse the conformational preference in this system.

There are three configurational possibilities for the enolates of symmetrical β-diketones, corresponding to combinations of E and Z configurations at the carbon–carbon partial double bonds.[15]

E,E-1 E,Z-1 Z,Z-1
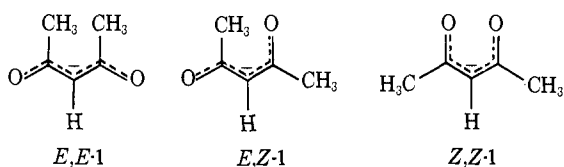
In contrast to analogous imides and anhydrides, the natural conformational preference of β-diketone enolates may be perturbed by interaction with their gegenions. Thus, while Z,Z-1 might be expected to suffer considerable destabilization from coulombic repulsion between the two proximate oxygen atoms, chelation to a metal ion might overcome any repulsive interactions and stabilize this configuration.

In order to control the influence of the counterion, we have examined the low-temperature spectra of sodium acetylacetonate in pyridine-d_5, a relatively poor solvator for Na^+, and have added different amounts of 18-crown-6[17] to complex with Na^+ and promote dissociation of the sodium enolate (Figure 1). The observation of two methyl singlets of different intensities at δ 2.09 and 2.38, as well as two methine singlets at δ 5.48 and 6.05, indicates the presence of E,E-1, and Z,Z-1 in equilibrium. If E,Z-1 were present, it should give rise to two equally intense singlets at temperatures where torsion about carbon–carbon partial double bonds is slow on the nmr time scale, and its presence in significant amounts can, therefore, be excluded. A straightforward assignment of configuration can be based upon the changes in peak ratios as a function of the crown ether concentration. Thus, an increase in the crown/enolate ratio from 1.6 (Figure 1a) to 3.7 (Figure 1c) decreases the intensity of the upfield methyl and methine singlets. These resonances must arise from Z,Z-1, whose concentration is lowered as a result of the decreased concentration of sodium ion available

Figure 1. Pmr spectra of sodium acetylacetonate in pyridine-d_5 containing 18-crown-6: a, $-50°$, crown/enolate ratio 1.6; b, $-44°$, crown/enolate ratio 1.6; c, $-50°$, crown/enolate ratio 3.7.

for complexation, and the low field singlet of each set must then be due to uncomplexed E,E-1.

The increased preference for E,E-1 in the absence of chelation of sodium ion is most likely related to the reduction of repulsive coulombic interactions between highly charged oxygen atoms, which is great enough to overcome significant 1,3-steric interactions between methyl groups. The nitrogen analog, diacetamide, which is neutral and has a more electronegative central atom, prefers the E,Z configuration,[12a] while the oxygen analog, acetic anhydride, adopts the Z,Z configuration preferentially.[18] The barriers to conformational interchange for related RCOXCOR systems are in the order expected for increased C–X double bond character as the electronegativity of X is reduced: formic anhydride,[13] X = O, 4.4 kcal/mol; diacetamide,[12a] X = NH, 10.8 kcal/mol; acetylacetonate anion, X = CH−, 12.9 kcal/mol.[19]

If we are correct in assuming that most of Z,Z-1 is associated with sodium ions and that there is a negligible amount of association for E,E-1, then the ratio of intensities of nmr signals also provides a mea-

(9) G. Bram, F. Guibé, and P. Sarthou, *Tetrahedron Lett.*, 4903 (1972).

(10) A. L. Kurts, A. Macias, I. P. Beletskaya, and O. A. Reutov, *Tetrahedron Lett.*, 3037 (1971).

(11) A. Mannschreck and H. Dvorak, *Tetrahedron Lett.*, 547 (1973).

(12) Imides: (a) E. A. Noe and M. Raban, *J. Amer. Chem. Soc.*, **95**, 6118 (1973); (b) A. Laurent, E. Laurent, and N. Pellissier, *Tetrahedron Lett.*, 2955 (1970).

(13) Formic anhydride: E. A. Noe and M. Raban, *J. Chem. Soc., Chem. Commun.*, 479 (1974).

(14) Pentadienide anions: W. T. Ford and M. Newcomb, *J. Amer. Chem. Soc.*, **96**, 309 (1974), and references cited therein.

(15) We feel that the use of the standard nomenclature for configuration at double or partial double bonds[16] is preferable to the use of the informal descriptive designations,[4] U, W, and sickle.

(16) J. E. Blankwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90**, 509 (1968).

(17) (a) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 7017 (1967); (b) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).

(18) H. J. Vledder, F. C. Mijlhoff, J. C. Leyte, and C. Romers, *J. Mol. Struct.*, **7**, 421 (1971).

(19) Complete line shape analysis at the coalescence temperature, $-21°$, afforded a first-order rate constant of 30 sec−1 for conversion of E,E-1 to Z,Z-1, which corresponds to a free energy of activation of 12.9 kcal/mol (54 kJ/mol). We regard $\Delta G^{\neq}$ as accurate to ± 0.2 kcal/mol (± 1 kJ/mol). The main source of error in the free energy of activation derives from the uncertainty in the sample temperature. Temperatures were measured with a copper–constantan thermocouple and are estimated to be accurate to $\pm 2°$.

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sure of the relative affinities for Na^+ of the enolate anion and 18-crown-6. The observed temperature dependence of the equilibrium ratios provides some support for this assumption. As the temperature is increased, the concentration of the unassociated E,E-1 isomer decreases dramatically. A temperature increase of only 6° lowers the percentage of E,E-1 from 30 to 23% (Figures 1a and 1b). In another experiment with the same crown/enolate ratio, the following percentages were observed as a function of temperature[20]: $-46°, 25\%; -51°, 32\%; -60°, 37\%; -65°, 41\%$. The direction of the temperature effect, to more unequal concentrations as the temperature is increased, points unequivocally to a significant entropy term. Apparently, the entropy requirements for complexation of Na^+ by 18-crown-6 and Z,Z-1 differ significantly. Because of its greater flexibility, 18-crown-6 exhibits substantially changed affinity for metal ions as a function of temperature.[21]

(20) These data fit a linear relationship between the logarithm of N, the peak ratio (E,E-1/Z,Z-1), and the reciprocal temperature (correlation coefficient, $r = 0.97$). If we assume an equilibrium of the form $LNa + C \rightleftharpoons CNa^+ + L^-$, where L^- represents the enolate anion and C, the crown ether, the equilibrium constant can be expressed as a function of N and R, the molar ratio of initial crown ether and sodium enolate concentrations: $K = N^2/(N(R - 1) + R)$. The plot of ln K vs. $1/T$ exhibited a comparable linearity ($r = 0.97$) since ln K is proportional to ln N for these values of N, and $R = 1.6$. An accurate determination of entropy and enthalpy as well as the exclusion of other possible equilibria will require more extensive data and is deferred to a subsequent detailed paper.
(21) We thank the National Science Foundation for support of this work.
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A Novel Case of Multiple Emissions from Nonthermally Equilibrated States of a Heterochelated Complex of Iridium(III)

Sir:

Measurements of luminescence decay curves of a vast majority of complexes of d^6 metal ions at 77°K reveal that the decays are simple, first-order processes. This indicates that the emissions are due to transitions from either a single level or a manifold of levels in thermal equilibrium.[1] Several unique heterotrischelated complexes of Rh(III) have recently been reported to show a departure from the normal exponential luminescence decays displayed by other d^6 metal ion complexes.[2] We wish to report a study of the luminescence decay of two heterobischelated complexes of Ir(III). One of these complexes, cis-dichloro-1,10-phenanthroline-2,2'-bipyridineiridium(III) chloride, [IrCl₂(phen)(bipy)]Cl, displays a nearly normal luminescence decay, which deviates only slightly from exponential behavior. The other, cis-dichloro-1,10-phenanthroline-5,6-dimethyl-1,10-phenanthrolineiridium(III) chloride, [IrCl₂(phen)-(5,6-Me(phen))]Cl, is found to have a distinctly non-

(1) J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, **92**, 7262 (1970); R. J. Watts, R. W. Harrigan, and G. A. Crosby, *Chem. Phys. Lett.*, **8**, 49 (1971); R. W. Harrigan, G. D. Hager, and G. A. Crosby, *ibid.*, **21**, 487 (1973); R. W. Harrigan and G. A. Crosby, *J. Chem. Phys.*, **59**, 3468 (1973); K. W. Hipps and G. A. Crosby, *Inorg. Chem.*, **13**, 1544 (1974).
(2) W. Halper and M. K. DeArmond, *J. Lumin.*, **5**, 225 (1972).

exponential luminescence decay. This latter complex represents the first case of multiple emissions from nonthermally equilibrated levels of an Ir(III) complex.

The two heterobischelated iridium(III) complexes were prepared by a modification of the method of Broomhead and Grumley,[3] and were characterized by elemental analysis, pmr, and infrared spectroscopy. The synthesis and characterization of the complexes are reported in detail elsewhere.[4] For this study, further tests for purity were made with thin-layer chromatography on Eastman 6062 Alumina Chromagram Sheet using ethanol for elution. The technique was demonstrated to be capable of resolving samples of the anticipated impurities, [IrCl₂(phen₂)]Cl and [IrCl₂-(bipy)₂]Cl, from the [IrCl₂(phen)(bipy)]Cl complex. No indication of either of these impurities could be detected in a thin-layer chromatogram of the heterobischelated complex, which appeared as a single spot on the plate. In the case of [IrCl₂(phen)(5,6-Me(phen))]Cl, the primary impurities were expected to be [IrCl₂(phen)₂]Cl and [IrCl₂(5,6-Me(phen))₂]Cl. The thin-layer technique was again found to be capable of resolving samples of these potential impurities from the heterochelated complex, which appeared as a single spot in a chromatogram. In order to check for photochemically induced impurities, aqueous solutions of the two heterochelated complexes were irradiated with a 1000-W Hg–Xe lamp (Hanovia 977B-1). The resulting products could be easily resolved from the starting material by thin-layer chromatography. No traces of these products were found in the complexes before irradiation.

The uv–visible absorption spectra of the two complexes were measured with a Cary 118 spectrophotometer and their corrected luminescence spectra were recorded with a Perkin-Elmer MPF-3 fluorescence spectrophotometer. The results are shown in Figure 1. In absorption, [IrCl₂(phen)(bipy)]Cl displays a spectrum which has characteristics of both [IrCl₂(phen)₂]Cl and [IrCl₂(bipy)₂]Cl. Similarly, the [IrCl₂(phen)(5,6-Me-(phen))]Cl absorption spectrum has bands found in the absorption of both [IrCl₂(phen)₂]Cl and [IrCl₂(5,6-Me-(phen))₂]Cl. Unlike the absorption spectra, the luminescence spectra of the two heterobischelated complexes have characteristics more similar to one of their homobischelated parents. The luminescence spectrum of [IrCl₂(phen)(bipy)]Cl has its first maximum at 21.1 kK, which is identical with the energy of the first emission maximum in both [IrCl₂(phen)₂]Cl and [IrCl₂(bipy)₂]Cl. The intensity distribution in the emission spectrum of this complex is nearly identical with that in [IrCl₂-(bipy)₂]Cl.[5] The luminescence spectrum of [IrCl₂-(phen)(5,6-Me(phen))]Cl has its first maximum at 20.6 kK compared to a value of 20.5 kK for [IrCl₂(5,6-Me-(phen))₂]Cl.[6]

The luminescence lifetimes of the two complexes were measured at 77°K in ethanol–methanol glasses (4:1, v/v). The complexes were excited at 337 nm with an Avco C950 pulsed nitrogen laser. The emission was passed through a Perkin-Elmer Model 98 monochromator equipped with a dense flint prism. Life-

(3) J. A. Broomhead and W. Grumley, *Inorg. Chem.*, **10**, 2002 (1971).
(4) R. J. Watts and J. S. Harrington, *J. Inorg. Nucl. Chem.*, in press.
(5) R. J. Watts and G. A. Crosby, *J. Amer. Chem. Soc.*, **93**, 3184 (1971).
(6) R. J. Watts, G. A. Crosby, and J. L. Sansregret, *Inorg. Chem.*, **11**, 1474 (1972).