

Figure 3. Emission spectra of transients and products for DDM obtained by OMA analysis. The spectra were recorded after N_2 purging the isooctane solution of a sample (1.0×10^{-4} M) which had previously been irradiated with 30 pulses at room temperature while saturated with O_2 . The dotted spectrum was obtained for benzophenone in N_2 -bubbled isooctane solution. The emission of benzophenone ketyl radical ($\lambda_{\max} \approx 560$ nm) was observed in addition to benzophenone phosphorescence ($\lambda_{\max} \approx 455$ nm).

Lamp photolysis of TPO under identical conditions does not lead to formation of TPE, DPA, or FL [undetectable by VPC and fluorescence analysis]. TPE is a product formed in flash- and low-temperature work; however, DPA, DPP, and FL are not reported.⁵

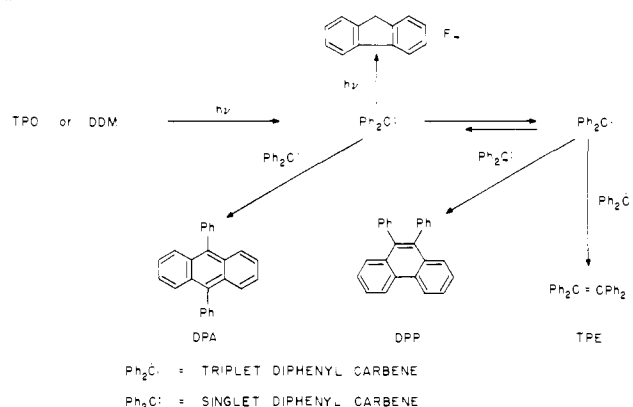
The yield of both DPA and FL increased markedly with increased laser power. Furthermore, the relative yield of DPA increased with increased concentration of carbene precursor while FL showed a contrasting behavior (Figure 2). The relative yield of DPP did not undergo a substantial change when either the substrate concentration or the laser intensity was varied.

The results of laser photolysis of O_2 -purged isooctane solutions of DDM (or TPO) are strikingly different (Figure 3) from those observed in N_2 -purged solution. Two new emissions that are virtually absent in samples which were N_2 purged during laser photolysis appear and are readily assigned to phosphorescence from benzophenone⁶ and to fluorescence from the diphenylketyl radical.⁷ Furthermore, the fluorescences of DPA and FL are now absent.

Although the chemical yields of these new products are low (as determined by VPC analyses of photolysis solutions⁸), they are of unique and unusual structure, and their production derives from the laser intensity; these products are absent in lamp photolysis. Work directed toward optimizing the conditions leading to their formation is now in progress.

Firm establishment of the details of the mechanism of formation of DPA, DPP, and FL must await the results of further experiments. However, we propose Scheme I at this time as a working, if somewhat speculative, mechanism that is consistent with our findings so far. First, the formation of TPE appears to occur predominately from dimerization of two triplet carbenes. This is consistent with the second-order decay of the DPC transient and the formation of TPE as a major product under flash-photolysis conditions. Second, the observation that the relative yield of FL decreases with respect to DPA as the number of absorbed laser photons increases (Figure 3) is consistent with production of FL from a first-order carbene reaction whereas DPA is produced from a path that is second order. Since formation of FL

Scheme I



is observed in the thermolysis of DDM and is typical of *singlet* carbene rearrangements, we propose that FL is produced from DPC singlet. Finally, since the response of DPP to the intensity of absorbed photons is different from both DPA and FL, we propose that DPP arises from either a triplet-singlet carbene dimerization or a triplet-triplet carbene dimerization. Control experiments suggest that the major portion of DPP formed does not arise from secondary photolysis of initially produced TPE.

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Direct Lanthanide-Induced-Shift NMR Determination of Conformer Populations in Substituted Cyclohexanones

Sir:

Shift reagents offer the possibility for the determination of conformer geometries and energies in solution¹ which would be difficult, if not impossible, by any other technique. Nevertheless, despite this promise, examples of the use of the lanthanide-induced shift (LIS) approach to the estimation of conformer energies are invariably either questionable in their analyses² or rely on other associated data³ (e.g., comparison of the LIS's in conformationally mobile molecules with the corresponding shifts in "rigid" systems).^{4,5}

(1) O. Hofer, *Top. Stereochem.* **9**, 111 (1976).

(2) For example, rotational isomerism in 2- and 3-carboxaldehydes of furan, pyrrole, and thiophene has been repeatedly investigated with LIS's. In none of these investigations were both the 1H and ^{13}C nuclei used, giving poorly determined systems (three equations in four unknowns). G. Gacel, M. C. Fournie-Zaluski, and B. P. Roques, *Org. Magn. Reson.*, **8**, 525 (1976); S. Nagata, T. Yanabe, K. Y. Yoshikawa, and H. Kato, *Tetrahedron*, **29**, 2545 (1973); G. Montaudo, S. Caccamese, V. Librando, and P. Maravigna, *ibid.*, **29**, 3915 (1973).

(3) J. A. Peters, J. D. Renijnse, A. V. D. Wiele, and H. V. Bekkum, *Tetrahedron Lett.*, 3065 (1971).

(4) K. L. Servis and D. J. Bowler, *J. Am. Chem. Soc.*, **95**, 3392 (1973).

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(6) Wolf, M. W.; Legg, K. D.; Brown, R. E.; Singer, L. A.; Parks, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 4490.

(7) Topp, M. R. *Chem. Phys. Lett.* **1976**, *39*, 423.

(8) After 100 pulses at 100 mJ, a 10^{-3} M N_2 -purged isooctane solution of precursor yielded 13.5% TPE, trace FL, and 0.2% TPA, and after 66 pulses at 100 mJ, a 10^{-5} M solution yielded 45.0% TPE, 0.8% FL, and trace TPA. The percent yield is 100 times the mole fraction of potential DPC present initially.

Table I. Coordinates and Populations for Substituted Cyclohexanone-Lanthanide Complexes^a

compd	$R \times 10^3$	r	ϕ	ψ	% populations		$-\Delta G$, kcal/mol	
					syn ^b	eq ^j	this study	other values
2-methyl	27	3.02	93	140	25	95	1.8 ± 0.3	$1.3,$ ^c $1.8,$ ^d $1.5,$ ^e $2.0,$ ^f 1.7 ^g
3-methyl	15	3.20	90	130	50	85	1.1 ± 0.1	$1.3,$ ^f 0.6 ^h
4-methyl	16	3.25	95	130	50	85	1.1 ± 0.2	$1.8,$ ^f 1.1 ^h
2-chloro	16	3.10	80	120	35	50	0.0 ± 0.1	0.08 ⁱ

^a Methylcyclohexanone-Yb complexes; chlorocyclohexanone-Eu complexes. ^b With the lanthanide syn to the substituent. ^c Reference 4. ^d B. Rickborn, *J. Am. Chem. Soc.*, **84**, 2414 (1962). ^e N. L. Allinger and H. M. Blatter, *ibid.*, **83**, 994 (1961). ^f W. D. Cotterill and M. J. T. Robinson, *Tetrahedron*, **20**, 765 (1964). ^g J. Cantacuzene, R. Jantzen, and D. Ricard, *ibid.*, **28**, 717 (1972). ^h P. J. Heyward, J. E. Rassing, and E. Wyn-Jones, *Adv. Mol. Relaxation Processes*, **6**, 307 (1975). ⁱ Reference 12. ^j Equatorial conformer.

We have recently shown that, by utilization of the LIS's for both ¹H and ¹³C nuclei, use of a physically reasonable model for lanthanide ion binding, and restriction of the number of variables defining the conformation of the system under study to a minimum, it is possible to refine, with considerable confidence, the solution conformations of a number of cyclic ketones, including cyclohexanone, 4-*tert*-butylcyclohexanone,⁶ and bicyclo[3.1.0]hexan-3-one.⁷ The conformations so obtained are in precise agreement with those obtained by other physical methods, where available, thus showing conclusively that in these cyclic ketones lanthanide complexation does *not* significantly perturb molecular conformation.

We now report that it is possible to extend this technique to the *direct* determination of conformer energies in solution. As previously, we restrict ourselves to cyclic ketones (2-, 3-, and 4-methylcyclohexanones and 2-chlorocyclohexanone) with only one functional group capable of complex formation. In these systems, the lanthanide binding model is well established, and there is good evidence that coordination to the lanthanide does not affect the conformational equilibria.⁸

LIS's were measured for all carbon (XL-100, 25.2 MHz) and hydrogen (R-34, 220 MHz) nuclei (on the same solutions) by incremental addition of Yb(fod)₃ to ca. 1 M solutions of the substrates in CDCl₃ (except for 2-chlorocyclohexanone, where only Eu(fod)₃-induced ¹H shifts were determined). The slopes of the plots of induced shift vs. the mole ratio of reagent to substrate (all correlation coefficients ≥ 0.999) were assumed to correspond to the bound shifts (ΔM values).

The basic geometry for the cyclohexanone skeleton was taken from a combined molecular mechanics and LIS investigation.⁶ Substituents were added with standard bond lengths and angles (C-C-C angles 111.0° for the methyl substituents). Apart from the positions of the substituents, the geometry of both chair conformers is identical. A computer program, LIRAS,⁹ was used to calculate expected ΔM values for all the carbon and hydrogen nuclei except for the carbonyl carbon (owing to its vulnerability to diamagnetic and contact shifts) and the methyl protons (averaging effects make these less sensitive to the conformational equilibria). The binding model used was the two-site model described previously,^{6,7} in which the lanthanide ion populates two sites symmetrically disposed with respect to the plane bisecting the C-CO-C angle. The calculated ΔM values were obtained as weighted means of the shifts for the two cyclohexanone conformers, i.e., for any nucleus B,

$$\Delta M_B^{\text{av}} = n_{\text{eq}} \Delta M_B^{\text{eq}} + n_{\text{ax}} \Delta M_B^{\text{ax}}$$

where n is the mole fraction. The lanthanide populations in the two binding sites, the mole fractions of the conformers, and the lanthanide coordinates (r , ϕ , and ψ)⁶ were scanned for minimum disagreement between calculated and observed LIS's, as estimated

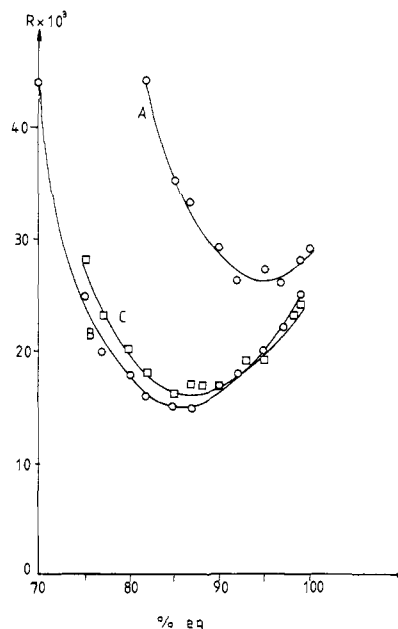


Figure 1. The agreement factor (R) vs. the percentage equatorial conformer in the LIS analysis of 2- (A), 3- (B), and 4- (C) methylcyclohexanones.

by a "crystallographic" agreement factor (R).

The results of these analyses are given in Table I and Figure 1. Of the four compounds, 4-methylcyclohexanone is by symmetry the least overdetermined, although there is one less degree of freedom since the binding sites must be equally populated. There are nine ΔM values, of which one is used for normalization, giving eight equations in the four unknowns, r , ϕ , and ψ , and the percentage equatorial conformer. The R value converges smoothly to a minimum of 0.016 for which 87% of the equatorial conformer is predicted.

3-Methylcyclohexanone is better determined (15 ΔM values), though in this case there are five unknowns as the lanthanide populations are not equal by symmetry. Interestingly, however, the global minimum is obtained with equal lanthanide populations. This is chemically reasonable as the 3-methyl group should have little effect on the relative availability of the carbonyl lone pairs.

It is in 2-methylcyclohexanone and 2-chlorocyclohexanone that the substituent is most likely to affect lanthanide binding at the carbonyl group. The derived lanthanide populations clearly reflect steric hindrance at the syn lone pairs (75 and 65%, respectively, of the lanthanide is on average on the side away from the substituent). The self-imposed limitations of our model may begin to break down in these cases. In particular, the assumption that the binding sites are symmetrically disposed with respect to the plane bisecting the C-CO-C angle may be questionable. However, if this assumption is not made, then in each case there will be at least eight unknowns (r , ϕ , and ψ for each site, plus lanthanide populations and conformer ratios) which would produce poorly determined systems. There is also no particular reason to favor a two-site model in a case where steric hindrance is large. In adamantane, it was necessary to adopt a symmetrical four-site model to obtain a good interpretation of the ΔM values.¹⁰

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(8) See ref 1, pp 160 and 182.

(9) An improved version of METALSEARCH^{9a} with the coordinate calculating routine of MODELBUILDER,^{9b} see L. Griffiths, Ph.D. Thesis, University of Liverpool, 1979. (a) L. O. Ford, Laboratory of Molecular Biophysics, University of Oxford. (b) J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967), QCPE Program No. 135.

In all the compounds studied here, the convergence of the program and the definition of the populations are good. The derived values of the free-energy differences between equatorial and axial conformers are given in Table I, along with errors at the 50% confidence limit¹¹ and literature values. The value of 1.3 kcal mol⁻¹ for the 2-methyl compound obtained by Servis and Bowler⁴ appears to be somewhat low. Interestingly, their treatment assumes that "the location of the lanthanide in the 2- and 4-alkylcyclohexanone complexes is the same"; in support of this they quote an earlier analysis of the LIS's of 4-*tert*-butylcyclohexanone which gave identical locations for the europium atom in the two cases on the basis of a one-site model.⁵ Our analysis clearly demonstrates the considerable differences in the lanthanide populations between the 2-methyl- and 4-methylcyclohexanones (and 4-*tert*-butylcyclohexanones) and emphasizes once again the errors which can arise from the use of the inadequate one-site

binding model. Particularly pleasing is the value for 2-chlorocyclohexanone. The conformational equilibrium in this molecule is solvent dependent: a recent study gave ΔG° varying from +1.0 (*n*-pentane) to -0.6 kcal mol⁻¹ (Me₂SO).¹² The literature value quoted in Table I is for the same solvent (CDCl₃) as was used in this LIS study and is in precise, though perhaps fortuitous, agreement with the value obtained here.

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Book Reviews*

Encyclopedia of Electrochemistry of the Elements. Volume XII. Edited by A. J. Bard (University of Texas) and H. Lund (University of Aarhus). Marcel Dekker, Inc., New York. 1978. xii + 512 pp. \$88 (\$75 by subscription).

This volume of the Encyclopedia is the second of five devoted to organic chemistry. Three have been published, and a fourth is in press. The three chapters in this book are devoted to Carbonyl Compounds (by D. H. Evans), Carboxylic Acids, Esters, and Anhydrides (by L. Ebersson and K. Nyberg), and Organic Sulfur Compounds (by J. Q. Chambers). Each chapter is subdivided into sections on electrode potentials and voltammetric properties, electrochemical (or mechanistic) studies and electrochemical synthesis, or applied electrochemistry.

The Series clearly represents an encyclopedia of the reactions which have been investigated electrochemically. No discussion of methods or apparatus is included. Much of the information is given in an extensive series of tables, although there is a concisely written discussion of general mechanistic details and specific points of interest. The editors have successfully managed to strike a good balance between analytical electrochemistry and preparative organic electrochemistry with a nice bridging through mechanistic studies. The precise balance, of course, does depend upon the orientation of the authors and does vary in these three chapters. The authors are all experts, both as chemists in their particular areas and as scientific writers.

The major problem in any encyclopedia is the selection of data to present within a reasonable number of pages. Most of the literature covered has appeared between the years of 1950 and 1974 with a few references before and after. However, references are given to earlier reviews and to books which summarize the older literature. The material chosen for discussion appears to be pertinent and meaningful, and the extensive tables make it possible to present a large number of results briefly. Thus, the selection seems to be exceptionally well made.

The Series was designed to provide a "natural starting point for new electrochemical investigations". This purpose is admirably served by this volume. The Series should be in all scientific libraries.

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Asbestos: Properties, Applications and Hazards. Volume I. Edited by L. Michaels and S. S. Chissick (University of London). John Wiley & Sons, New York. 1979. xi + 553 pp. \$62.50.

Although the use of flame-resistant asbestos cloth in classical antiquity and medieval China are attested to by Pliny the Elder and Marco Polo, respectively, it was the spread of the steam engine during the Industrial Revolution that transformed asbestos from a curiosity to an important insulating material. Subsequently produced in bulk—often under ap-

palling conditions—asbestos production has increased from 50 tons in 1877 to over 3 000 000 tons in 1977. Over 90% of this material is chrysotile asbestos, a fibrous serpentine hydrated magnesium silicate. Increasing reports of asbestos-related pulmonary fibrosis (asbestosis) during the 1930-40s, and neoplasia during the 1950-60s, have resulted in considerable public concern and increased governmental regulation.

The present book would bring together a wide variety of material "of value to all concerned with the asbestos industry ... and the general public", primarily from a British point of view; indeed, all but two of the 16 articles are by British authors. The Introduction provides a useful glossary, a brief history of British regulation, and a 27-page annotated list of commercially available products and services in Britain. The chapters on mineralogy, chemistry, and physics of asbestos are on the whole attractive and useful introductions, although the problem of non-fibrous asbestos analogues is not sufficiently dealt with.

The clinical and histopathological aspects of asbestos-related disease are well illustrated and dealt with at length, although there is comparatively little discussion of possible mechanisms. The 57-page chapter on "Attitudes to Asbestos" is an over-detailed, rather unexciting comparison of government and industry positions; it includes many pages of verbatim quotes from the "Medical Examination" policy of a producer, the 1975 OSHA proposed regulations, proposed revisions by Johns-Manville, and a chart of claims and counterclaims on health effects. This and the chapters on industrial asbestos fiber usage, work practices, control, and replacement may be useful to concerned industrialists but may be of less interest to the "general public".

Unfortunately, these enthusiasms are balanced by a slighting of other topics of importance, especially, those representing new technical trends. For example, there are only four pages on electron microscopic identification—the topic of two major published symposia by U.S. regulatory agencies (FDA, 1976; NBS, 1977) and the technical key to future monitoring requirements—and only one page is devoted to *in vitro* effects, which may eventually provide a useful correlation with (and thus screening method for) adverse health effects. Similarly, despite 140 pages on health effects, mostly devoted to human studies (where accurate characterization of materials, exposures, and controls is difficult), there is virtually no mention of the important work of Stanton, Wright, and other U.S. investigators on the apparently crucial relationship between fiber morphology and carcinogenicity. Such material was available in 1978, although, in all fairness, it may be part of the planned, second volume.

Despite claims of a wider potential readership, this volume appears primarily an attractive, somewhat dated, text that seeks to provide practical, down-to-earth background material and where-to-find-it advice for industrially oriented readers. Although its British emphasis may limit its usefulness for some American readers, it does provide an interesting

*Unsigned book reviews are by the Book Review Editor.