The *in-phase* combination of the two triplet configurations and the singlet ground state are then coupled by a spin-orbit term which is proportional to $2\langle\sigma_A|H_{SO}|\pi_A\rangle$. On the other hand the two equal one-center integrals occurring in the coupling between the *out-of-phase* combination of the two triplet configurations and the ground state cancel each other. Note also that this second combination is much higher in energy and certainly does not cross the G_s surface.

(15) R. M. Hochstrasser, H. Lutz, and G. W. Scott, *Chem. Phys. Lett.*, **24**, 162 (1974).

(16) The lifetime of a transition state is generally taken to be 10^{-12} to 10^{-13} sec for relatively simple molecules: A. A. Frost and R. G. Pearson "Kinetics and Mechanism", Wiley, New York, N.Y., 1965, p 77.

(17) As pointed out by one of the referees the π molecular orbital of acetone may be approximately described as $(\sigma_A + \sigma_C)/\sqrt{2}$. The term which couples $^3\sigma_A\pi_B$ and $^1\sigma_A\sigma_B$ then becomes $\frac{1}{2}\langle\sigma_A|H_{SO}|\pi_A\rangle$. Since the probability of a radiationless transition is proportional to the square of the electronic (spin-orbit) coupling term,[6] the probability of the $T_a \rightarrow G_s$ transition will be roughly one-fourth of the $G_s \rightarrow T_a$ transition probability.

(18) P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 3025 (1973).

(19) The pattern of states displayed in Figure 2a is confirmed by MINDO/3 calculations. See M. J. S. Dewar, S. Kirschner, and H. W. Kollmar, *J. Am. Chem. Soc.*, **96**, 7579 (1974).

(20) J. Birks, "Photophysics of Organic Hydrocarbons", Wiley, New York, N.Y., 1970.

(21) N. J. Turro and H. C. Steinmetzer, *J. Am. Chem. Soc.*, **96**, 4679 (1974).

(22) For example there is no one-center term coupling the singlet and triplet $n\pi^*$ states in aliphatic ketones. Still the rate of the corresponding radiationless intersystem crossing is large (10^7 sec^{-1}).

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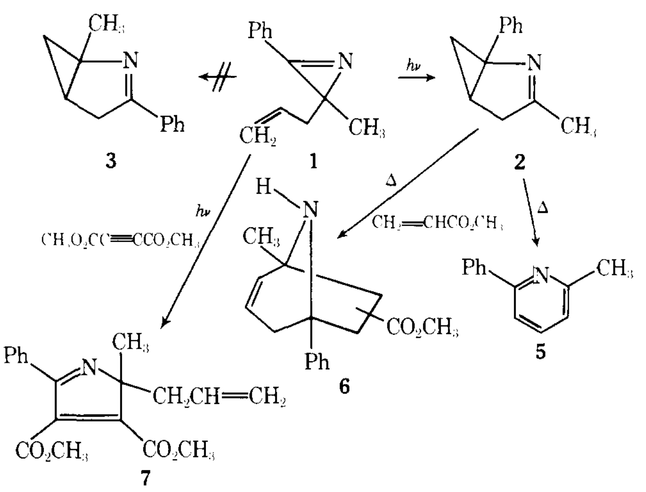
1,1-Cycloaddition from a 1,3-Dipole[1]

Sir:

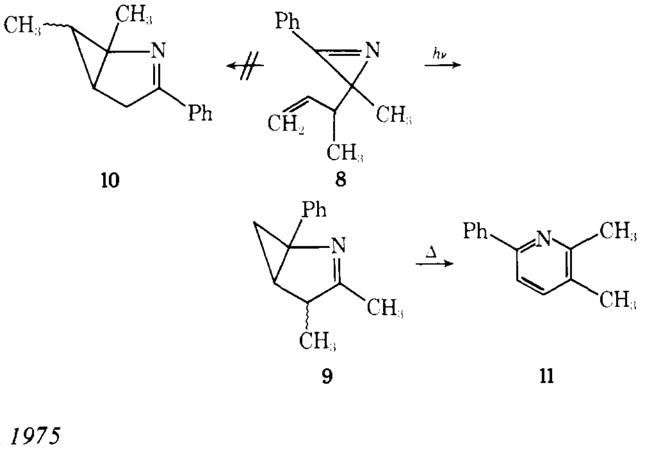
Huisgen and coworkers were the first to recognize fully the general concept and scope of 1,3-dipolar cycloadditions,[2-4] a reaction of considerable merit for the synthesis of five-membered heterocyclic rings. Our research group has recently investigated the 1,3-dipolar cycloaddition reactions of nitrile ylides generated by photolysis of arylazirines.[5,6] Nitrile ylides may be classified as nitrilium betaines, a class of 1,3 dipoles containing a central nitrogen atom and a π-bond orthogonal to the 4π-allyl system. Among the possible resonance forms of a nitrile ylide, a carbene structure can be envisioned which makes conceivable a 1,1 cycloaddition of this 1,3 dipole.[7] We report herein the first example of such a cycloaddition.

In order to establish the orientation of the intramolecular 1,3-dipolar cycloaddition reactions of nitrile ylides, we chose to investigate the photochemistry of 2-phenyl-3-methyl-3-allylazirine (**1**).[8] When a thoroughly deaerated solution of **1** was irradiated in cyclohexane with light of wavelength >250 nm, an extremely rapid and clean conversion to 1-phenyl-3-methyl-2-azabicyclo[3.1.0]hex-2-ene (**2**) was observed. The identity of **2** was determined by its straightforward spectral characteristics [ir (neat) 1640 cm^{-1}; NMR (100 MHz) τ 9.64 (t, 1 H, J = 5.0 Hz), 8.68 (dd, 1 H, J = 8.0 and 5.0 Hz), 8.33 (m, 1 H), 8.13 (s, 3 H), 7.64 (d, 1 H, J = 17.5 Hz), 7.22 (dd, 1 H, J = 17.5 and 8.0 Hz), 2.61-3.10 (m, 5 H)] as well as its facile conversion to 2-methyl-6-phenylpyridine (**5**) (picrate 131-132°)[9] on heating. When the thermolysis of azabicyclohexene **2** was carried out in toluene in the presence of methyl acrylate, azabicyclo[3.2.1]octene (**6**); mp 87-88°, was isolated in good yield [NMR (100 MHz) τ 8.68 (s, 3 H), 7.76 (dd, 1 H, J = 18.0 and 4.0 Hz), 7.48 (m, 3 H), 6.82 (dd, 1 H, J = 7.0 and 4.0 Hz), 6.36 (s, 3 H), 4.34 (ddd, 1 H, J = 9.5, 4.0, and 2.0 Hz), 4.14 (dt, J = 10.0 and 1.5 Hz), 2.4-2.8 (m, 5 H)]. The formation of this adduct is readily interpreted if it is assumed that **2** undergoes an initial 1,3-proton shift to give 1-phenyl-3-methyl-2-azabicyclo[3.1.0]hex-3-ene which subsequently undergoes cycloaddition with the added dipolarophile. Tanny and Fowler[10] have recently shown that the 2-azabicyclo[3.1.0]hex-3-ene ring system will undergo thermal cycloaddition reactions with electron-deficient olefins, thereby providing good analogy for the last step of the proposed sequence.



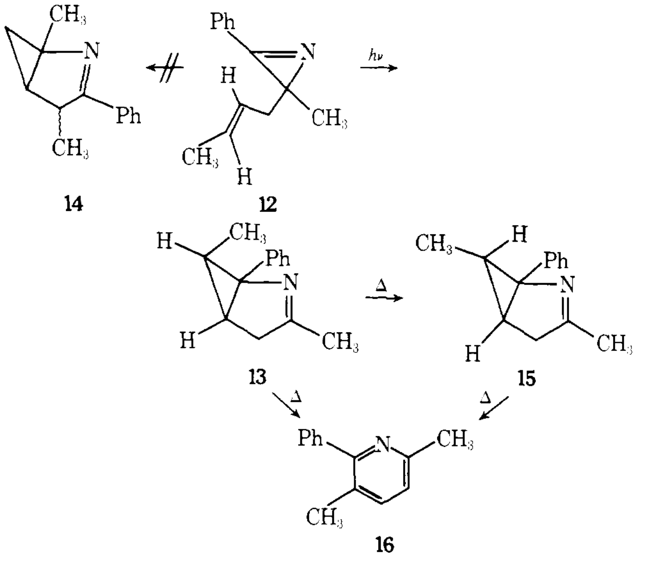
The ultraviolet spectrum (cyclohexane) of the photoproduct showed a maximum at 225 nm which is compatible with structure **2** but not with the isomeric azabicyclohexene **3**.[11] Photolysis of **1** in the presence of excess dimethyl acetylenedicarboxylate resulted in the trapping of a nitrile ylide and afforded cycloadduct **7**, mp 58-60°, in high yield. Under these conditions, the formation of **2**, which is produced in quantitative yield in the absence of a trapping reagent, is entirely suppressed.[12,13] Similar results were obtained when methyl acrylate was used as the trapping reagent.

The photoreactions of the closely related methyl-substituted azirines **8** and **12** were also studied in order to assess the generality of the photocycloaddition reaction. Irradiation of **8** in cyclohexane afforded a quantitative yield of 1-phenyl-3,4-dimethyl-2-azabicyclo[3.1.0]hex-2-ene (**9**) as a mixture of endo (25%) and exo (75%) isomers. The NMR of the major isomer [(100 MHz) τ 9.62 (t, 1 H, J = 4.6 Hz), 8.92 (d, 3 H, J = 8.0 Hz), 8.66 (dd, 1 H, J = 8.0 and 4.6 Hz), 8.42 (dd, 1 H, J = 8.0 and 4.6 Hz), 8.12 (s, 3 H), 7.48 (1 H, q, J = 8.0 Hz), 2.4-3.0 (m, 5 H)] showed the two cyclopropyl protons expected for structure **9** but not for the isomeric azabicyclohexene **10**.[14] The initial photoproduct was smoothly converted to 2,3-dimethyl-6-phenylpyridine (**11**) on heating. Structure **11** was verified by comparison with an authentic sample.[15] The formation of **9** could be completely suppressed when the irradiation of **8** was carried

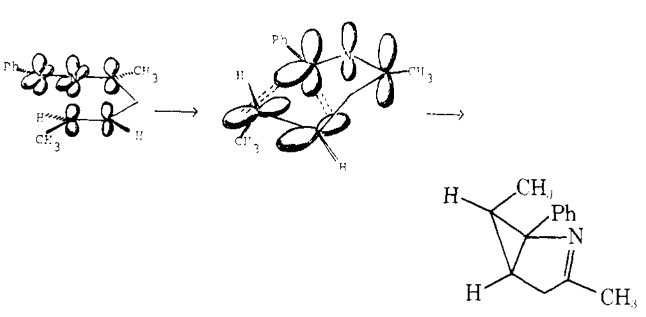


out in the presence of excess methyl acrylate.[13] The only product formed under these conditions was the usual Δ^1-pyrroline.[5]

When 2-phenyl-3-methyl-3-crotylazirine (**12**) was irradiated in cyclohexane, a single photoproduct (**13**) was initially obtained. The structure of this material was readily established by NMR spectroscopy. The NMR spectrum of **13** consisted of a methyl doublet at τ 9.24 (J = 6.0 Hz), a one proton doublet of quartets at τ 8.42 (J = 8.0 Hz), a triplet at τ 8.13 (J = 8.0 Hz), a singlet at τ 8.00 (3 H), a doublet at τ 7.80 (1 H, J = 18.0 Hz), a well-defined doublet of doublets at τ 7.26 (1 H, J = 18.0 and 8.0 Hz), and a multiplet for the aromatic protons at τ 2.4–3.0 (5 H). The characteristic ABX pattern for the protons located at C_4 and C_5 clearly eliminates the alternative azabicyclohexene **14**. *Most importantly, the magnitude of the cyclopropyl hydrogen coupling (J = 8.0 Hz) indicates a cis relationship of the protons and thus requires that the 6-methyl group in* **13** *be endo.* The initial photoproduct slowly epimerized to the thermodynamically more stable exo isomer (**15**) at room temperature.[16] On standing for longer periods of time, both isomers were converted to 2,5-dimethyl-6-phenylpyridine (**16**).[15]



Concerted 1,3-dipolar additions are known to proceed via a "two-plane" orientation complex in which the dipole and dipolarophile approach each other in parallel planes.[2-4] In order to achieve this type of transition state, the linear nitrile ylide must first bend. This involves disruption of the orthogonal π bond at some modest energy cost but leaves the allyl anion π system undisturbed. The cycloaddition of azirines **1**, **8**, and **12** with added dipolarophiles proceeds in this fashion affording Δ^1-pyrrolines as the primary cycloadducts (e.g., **7**). Inspection of molecular models of the allyl-substituted nitrile ylides indicates that the normal "two-plane" orientation approach of the linear nitrile ylide and the allyl π system is impossible as a result of the geometric restrictions imposed on the system. Product formation is possible, however, if the linear nitrile ylide undergoes rehybridization to give a species of bent geometry[17] which subsequently undergoes 1,1 cycloaddition with the neighboring double bond. The most favorable transition state for the 1,1-cycloaddition reaction is one in which the π orbitals of the nitrile ylide and olefinic double bond are orthogonal. This orthogonality permits the occurrence of an orbital symmetry-allowed [$\omega_s^2 + \pi_a^2$] process and thus accommodates the formation of the thermodynamically less favored endo isomer (**13**).[18] It should be pointed out that this is the first example of the addition of a carbene to an olefin which proceeds with complete inversion of stereochemistry about the π system.



We are continuing to explore the scope and mechanistic details of this novel 1,1-cycloaddition reaction.

Acknowledgment. We gratefully acknowledge the National Science Foundation (Grant PO-37550) and Merck Sharp and Dohme for their generous support of this work.

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(4) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes", S. Patai, Ed., Interscience, N.Y., 1964, pp 806–878.

(5) A. Padwa and J. Smolanoff, *J. Am. Chem. Soc.*, **93**, 548 (1971); A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *ibid.*, **94**, 1395 (1972); *ibid.*, **95**, 1945, 1954 (1973); *Pure Appl. Chem.*, **33**, 269 (1973); A. Padwa and S. I. Wetmore, *J. Org. Chem.*, **38**, 1333 (1973); **39**, 1396 (1974); *J. Am. Chem. Soc.*, **96**, 2414 (1974); A. Padwa, D. Dean, and J. Smolanoff, *Tetrahedron Lett.*, 4087 (1972); A. Padwa, J. Smolanoff, and A. Tremper, *ibid.*, 29, 33 (1974).

(6) N. Gakis, M. Marky, H. J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 748 (1972); H. Giezendanner, M. Marky, B. Jackson, *ibid.*, H. J. Hansen, and H. Schmid, *ibid.*, **55**, 745 (1972); B. Jackson, M. Marky, H. J. Hansen, and H. Schmid, *ibid.*, **55**, 919 (1972).

(7) R. Huisgen, R. Sustmann, and K. Bunge, *Chem. Ber.*, **105**, 1324 (1972), have shown that three-membered rings are not primary products in the 1,3-dipolar cycloadditions leading to five-membered heterocycles with both nitrilium and diazonium betaines.

(8) Azirine **1** was prepared by a modified Neber reaction in which 1-phenyl-2-methyl-4-penten-1-one was treated with dimethylhydrazine according to the general procedure of N. J. Leonard and B. Zwanenburg, *J. Am. Chem. Soc.*, **89**, 4456 (1967). This same approach was used to prepare azirines **8** and **12**. Complete spectroscopic properties of the unsaturated azirines will be given in our full publication.

(9) The structure of 2-methyl-6-phenylpyridine (**5**) was established by comparison with an independently synthesized sample prepared by treating 2-methylpyridine with phenyllithium, J. M. Bonnier, J. Court, and T. Fay, *Bull. Soc. Chim. Fr.*, 1204 (1967).

(10) S. R. Tanny and F. W. Fowler, *J. Org. Chem.*, **39**, 2715 (1974).

(11) The uv spectra of 2-phenyl-substituted Δ^1-pyrrolines show a maximum at 240 nm, whereas 2-methyl-substituted Δ^1-pyrrolines absorb at 221 nm: R. Bonnett, *J. Chem. Soc.*, 2313 (1965).

(12) *Control experiments showed that photoadduct* **2** *does not undergo photocycloaddition with dimethyl acetylenedicarboxylate or with methyl acrylate.*

(13) The fact that photolysis of these allyl-substituted azirines affords a nitrile ylide intermediate which could be trapped by an external dipolarophile (i.e., as **7**) eliminates a [2 + 2] cycloaddition of the azirine C=N bond with the olefin and subsequent rearrangement of a hypothetical azatricyclo[$2.2.0^{1,4}0^{2,6}$]hexane intermediate as the mechanism for the formation of the azabicyclo[3.1.0]hex-3-ene system.

(14) The NMR of the minor isomer contained a one-proton pentuplet at τ 6.80 (J = 8.0 Hz) which is only consistent with the endo stereochemistry of azabicyclohexene **9**.

(15) Dimethylphenylpyridines **11** and **16** were compared with the spectra of authentic samples: J. M. Bonnier and J. Court, *Bull. Soc. Chim. Fr.*, 142 (1970). We thank Professor Court for supplying us with copies of the NMR and ir spectra.

(16) The NMR spectrum of the exo isomer **15** showed a 4.5-Hz trans coupling constant for the cyclopropyl hydrogens after double irradiation.

(17) Salem has recently carried out some ab initio computations on the ground and excited-state energy surfaces of the 2*H*-azirine molecule which indicate that the ring opened intermediate is capable of dual reactivity when intercepted by an added dipolarophile: L. Salem, *J. Am. Chem. Soc.*, **96**, 3486 (1974).

(18) An alternate explanation is that the 1,1-cycloaddition process occurs by initial attack of the carbene carbon onto the terminal position of the double bond. Such an attack will generate a six-membered ring dipole which contains a secondary carbonium ion as well as an azaallyl anion portion. Collapse of this new 1,3-dipole to the thermodynamically favored exo product will result in a severe torsional barrier on closure. On the other hand, collapse to the thermodynamically less favored endo isomer moves the phenyl and methyl groups increasingly further apart and could account for the formation of the less stable product. The major flaw with this rationale, however, is that initial bond formation should occur via a five-membered ring since the methyl group on the terminal position would be expected to stabilize the incipient carbonium ion generated. Further work with other terminally substituted olefins is in progress and should clarify this point.

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Pressure Effects on Conformational Equilibrium in Solution. Infrared Studies of Halocyclohexanes

Sir:

Present knowledge of the effects of pressure on chemical equilibrium is very limited. Inherently, such information would be valuable in improving our understanding of the properties of dissolved molecules; data from pressure studies could supplement the many important results obtained from investigations of solvent and temperature effects on chemical equilibrium. Since high pressure spectral techniques have been available for several decades,[1] it is surprising that there have been so few careful studies of solutions at high pressure. In particular, we can find no quantitative spectral investigations of conformational equilibria at increased pressures. A major reason for the scarcity of quantitative solution results is probably the difficulty of measuring pressures in compressed liquid samples.

Numerous compounds existing as mixtures of conformers have vibrational modes (fundamentals and combinations) for each conformer which give rise to distinct, well-separated bands in the infrared or Raman spectra. For example, many bands in the spectra of halocyclohexanes (in the 1500–100-cm^{-1} region) have been assigned to axial or equatorial forms.[2] Variations in temperature or solvent can induce changes in conformational equilibria, and quantitative intensity studies of certain vibrations have been used to infer changes in equilibrium constants.[3] We are at present using a related approach to investigate the effects of pressure on conformational equilibria and report here quantitative results for dilute solutions of chlorocyclohexane, *trans*-1,4-dichlorocyclohexane, and *trans*-1,4-dibromocyclohexane in carbon disulfide.

Infrared spectra have been recorded using the diamond anvil cell,[1] at a temperature approximately 50°.

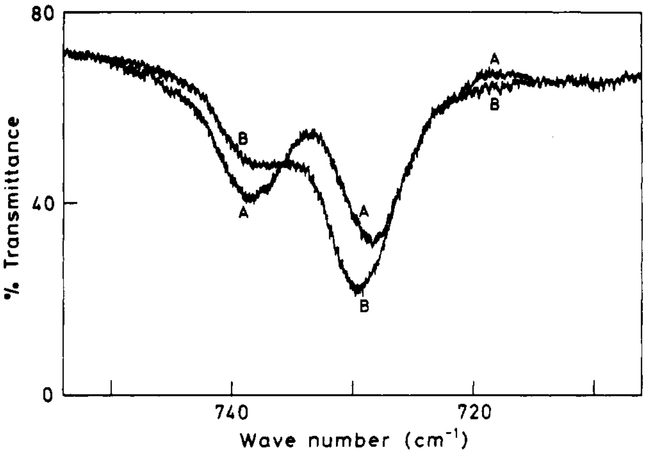

Figure 1. Infrared active C–Br stretching modes of the diequatorial (738) and diaxial (728 cm^{-1}) conformers of *trans*-1,4-dibromocyclohexane (CS_2 solution, 0.12 *M*); pressure, curve (A) 0.4 and curve (B) 6.7 kbar. Corresponding bands in chlorocyclohexane at 732 (e) and 685 cm^{-1} (a) and *trans*-1,4-dichlorocyclohexane at 783 (ee) and 758 cm^{-1} (aa) were employed for the calculations.

Table I. Changes in Conformational Populations with Pressure, and Differences in Partial Molar Volumes

Solute	% increase in K per kbar[a, b]	$\Delta\bar{V}$ (cm^3/mol)[b, c]
Chlorocyclohexane	7.3 ± 0.4	−1.87 ± 0.14
trans-1,4-Dichlorocyclohexane	11.5 ± 0.6	−2.8 ± 0.2
trans-1,4-Dibromocyclohexane	15.4 ± 0.6	−3.8 ± 0.2

[a] K = [axial]/[equatorial]. [b] Calculated for each compound from least-squares parameters obtained by fitting data to the linear integrated form of eq 1. Approximately 20 intensity ratio measurements were made for each system in the pressure range from 0 to 10 kbar. Uncertainties in reported values are least-squares estimates of standard deviations. [c] Volume changes for conversion of equatorial to axial forms.

In determining pressures of liquid samples in the diamond cell, we have found it convenient to use infrared results reported by Drickamer and coworkers.[4] They found that O–H stretching frequencies of alcohols and carbonyl overtone frequencies of ketones dissolved in organic solvents are considerably red-shifted with increased pressure. Thus, an internal standard (such as methanol or cyclohexanone) can be added in small concentrations along with compounds to be studied in CS_2 or other organic solvents. From measurement of the O–H or C=O (overtone) frequencies of the standard (in the 3600- and 3400-cm^{-1} regions, respectively) pressures in the 0–12 kbar range can be determined directly. In a number of the cyclohexane systems, the CH_2 deformation modes (at about 870 cm^{-1}) are also fairly pressure sensitive, and changes in these frequencies can be correlated with those in the compounds studied by Drickamer et al.

By studying pressure effects on the spectra of dilute solutions of several mono- and dihalocyclohexanes in CS_2, we have observed that the conformational equilibria shift markedly in the direction of increased populations of the axially substituted conformers. The bands which are assigned to the e (or ee) species diminish considerably in intensity, whereas the a (or aa) bands increase. For quantitative purposes we have measured integrated intensities of the infrared active C–X stretching bands (X = Cl or Br) in CS_2 solutions containing a few mole per cent of the individual cyclohexane derivatives; pressures have been varied from 0 to about 10 kbar. Figure 1 shows infrared curves for a dilute solution of *trans*-1,4-dibromocyclohexane in CS_2 in the 710–750-cm^{-1} region. We assume that the respective band areas are proportional to concentrations of the conformers; thus the conformational equilibrium constant (K = [axial]/[equatorial]) is taken to be directly proportional to the ratio of the axial to the equatorial band areas. Values of the change in conformer partial molar volume (equatorial to axial) are inferred from the relation

$$\Delta\bar{V} = -RT\,\mathrm{d}\ln K/\mathrm{d}P \qquad (1)$$

Table I summarizes least-squares values of changes in conformational population and partial molar volume for the three halocyclohexanes.

Volume changes reported here (−1.87 to −3.8 cm^3/mol), for conversion of equatorial into axial forms, are similar in magnitude to those estimated from proton NMR and ultra-