Schaad, "Hydrogen Bonding", Marcel Dekker, New York, N.Y., 1974.

(2) (a) A. S. N. Murty and C. N. R. Rao, *J. Mol. Struct.*, **6**, 253 (1970); (b) P. A. Kollman and L. C. Allen, *Chem. Rev.*, 72, 283 (1972).

(3) (a) G. Karlström, H. Wennerström, B. Jonssön, S. Forsén, J. Almlöf, and B. Roos, *J. Am. Chem. Soc.*, **97**, 4188 (1975); (b) A. Johansson, P. Kollman, and S. Rothenberg, *Chem. Phys. Lett.*, **18**, 276 (1973); (c) J. E. Del Bene and W. L. Kochenour, *J. Am. Chem. Soc.*, **98**, 2041 (1976).

(4) (a) S. Yamabe and K. Morokuma, *J. Am. Chem. Soc.*, **97**, 4458 (1975); (b) A. D. Isaacson and K. Morokuma, *ibid.*, **97**, 4453 (1975).

(5) J. E. Del Bene, *J. Am. Chem. Soc.*, **95**, 6517 (1973), and references cited therein.

(6) (a) P. A. Kollman and L. C. Allen, *J. Am. Chem. Soc.*, **93**, 4991 (1971); (b) P. A. Kollman, J. F. Liebman, and L. C. Allen, *ibid.*, **92**, 1142 (1970).

(7) P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969).

(8) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(9) K. Siegbahn, C. Nordling, G. Johannsson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, 1969.

(10) (a) R. S. Brown, *Can. J. Chem.*, **54**, 642 (1976); (b) *ibid.*, **54**, 1929 (1976); (c) *ibid.*, in press.

(11) (a) J. S. Wieczorek, T. Koening, and T. Balle, *J. Electron Spectrosc. Relat. Phenom.*, **6**, 215 (1975); (b) S. Leavell, J. Steichen, and J. L. Franklin, *J. Chem. Phys.*, **59**, 4313 (1973); (c) R. K. Thomas, *Proc. R. Soc. London, Ser. A.*, **331**, 249 (1972).

(12) The program ELSPEC is an adapted version of the Lawrence Berkeley Laboratories SUNDER program for deconvoluting spectra.

(13) S. L. Friess and H. D. Baldridge, *J. Am. Chem. Soc.*, **78**, 2482 (1956).

(14) C. J. Allan, U. Gelius, D. A. Allison, G. Johansson, H. Siegbahn, and K. Siegbahn, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 131 (1972).

(15) P. Finn, R. K. Pearson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **10**, 378 (1971).

(16) (a) R. L. Martin and D. A. Shirley, *J. Am. Chem. Soc.*, **96**, 5299 (1974); (b) D. W. Davis and J. W. Rabalais, *ibid.*, **96**, 5305 (1974); (c) B. E. Mills, R. L. Martin, and D. A. Shirley, *ibid.*, **98**, 2580 (1976).

(17) (a) P. J. Krueger and H. D. Mettee, *Can. J. Chem.*, **43**, 2970 (1965) report that for the ethanolamines, the OH···N form is 1–2 kcal/mol more stable in solution than the NH···O form. (b) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **95**, 693 (1973).

(18) An ab initio calculation of β-hydroxyacrolein in the C_s (t) (non-H-bonded) and C_s (c) (H-bonded) conformations shows that the H bond induces a shift of 0.8 eV in the hydroxyl oxygen and −0.7 eV in the carbonyl oxygen, in agreement with our experimental observations reported here. J. E. Del Bene, private communication.

(19) T. Koopmans, *Physica*, **1**, 104 (1934).

(20) For example, the charge-density plot for $(HF)_2$ shows the charge density actually increasing on the H involved in the H bond, while a population analysis leads one to the opposite conclusion (ref 7).

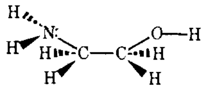
(21) (a) D. T. Clark, D. Kilcast, D. B. Adams, and W. K. R. Musgrave, *J. Electron Spectrosc. Relat. Phenom.*, **6**, 117 (1975); (b) D. T. Clark, D. Kilcast, and W. K. R. Musgrave, *Chem. Commun.*, 516 (1971).

(22) D. W. Davis, D. A. Shirley, and T. D. Thomas, *J. Am. Chem. Soc.*, **94**, 6565 (1972).

(23) The program used was a standard CNDO/2 package modified at the Lawrence Berkeley Laboratory as described in ref 22, and was kindly supplied by Professor R. G. Cavell. Although the approach is similar to that of eq 1, it is not identical and incorporates no empirical parameters outside the CNDO/2 approach. Standard bond lengths and angles given by J. A. Pople and M. Gordon [*J. Am. Chem. Soc.*, **89**, 4253 (1967)] were assumed.

(24) The choice of the orientation of the O–H bond in **21** is arbitrary and its only significance is that it is non-H-bonded and gauche to the methylene unit. Clearly the amino group may prefer to be gauche to its methylene unit as well, but we have chosen the eclipsed conformation to probe those charge distributions actually arising from H-bond formation, and not from rotations about bonds.

(25) Rotation about the C(1)–C(2) bond produces conformations of differing energy in the absence of H bonding. In fact, our calculations on **22** and its non-H bonded conformation **22a**, in which only the O–H bond has been reoriented 180°, show population shifts similar to but reduced in magnitude to those between **21** and **22**. Although their energies are nearly equal, the CNDO/2 computed potentials for **22** and **22a** parallel those for **22** and **21**.



22a

(26) On the expectation that ion state relaxation should be important for H-bonded systems, we have attempted to use a relaxation potential model (RPM) to calculate the excited-state effect of removal of a core electron. Such computations[16a] give results which parallel those obtained using only the ground state of the molecule. We feel, however, that the limitations imposed by the present CNDO/2 calculations with respect to orbital occupancy should invalidate RPM calculations for systems containing lone pairs of similar energies.

High-Pressure High-Resolution Nuclear Magnetic Resonance. Pressure Dependence of the Ring Proton Chemical Shifts of Substituted Benzenes

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Abstract: Pressure dependence of the ring proton chemical shifts of 1,4-disubstituted benzenes relative to the internal benzene has been measured in n-hexane up to 2000 kg cm^{-2} using a 100-MHz high-resolution spectrometer. The observed displacement of the proton resonance to high field, with increasing pressure, has been interpreted in terms of the substituent steric effect, which hinders partly the approach of medium molecule to the resonating proton ortho to the substituent.

Most of the liquid organic compounds, when compressed to a pressure region of the order of 10^3 kg cm^{-2}, are forced to lose 10–15% of their volumes at 1 atm with the resultant contraction of intermolecular separations. This contraction intensifies the contacts between medium molecules and hydrogen atoms which are located normally on the surfaces of the organic molecules, giving rise to change in the so-called medium effect on the proton magnetic resonance. The high-pressure high-resolution proton NMR[1,2] thus appears to be a very attractive means for studying the behavior of the organic molecule under high pressure. In preceding papers, we reported the high-resolution NMR experiments under the increased pressures up to 2000 kg cm^{-2} carried out on a standard high-resolution spectrometer[1b,d,e] operating at 60 MHz with some observations on the pressure dependence of proton chemical shifts of organic compounds.[1b,d] The results were qualitatively discussed in terms of the pressure effect on the intermolecular interactions. Since we are using the internal referencing system throughout this experiment with a reference compound dissolved in a sample solution and subjected to the influence of the same high pressure, the only detectable pressure effect is the difference of the pressure effects on the chemical shifts between the sample and reference compounds, to which we refer hereafter as the "relative pressure shift", $\delta\Delta$. Although the relative pressure shifts of the proton resonances are shown to be generally small[1b,d] and are the order of magnitude 1–5 $\times$ 10^{-2} ppm under the increased pressures up to 2000 kg cm^{-2}, our technique to measure the shifts with a considerable accuracy of $\pm 3 \times 10^{-3}$ ppm (with a 60-MHz spectrometer) or that of $\pm 1 \times 10^{-3}$ ppm (with a 100-MHz spectrometer used in the present study) proved to be satisfactory in detecting the small differences of the shifts between differently behaving protons on the molecules and was shown to be useful in the study of intermolecular interactions at high pressure. The present report represents an effort to examine the effect of the increased pressure on the chemical shift of the aromatic ring proton located ortho to the substituent which might sterically hinder the approach of the medium molecules to the ortho proton. We have chosen the nearly spherically symmetric substituents for the present purpose. For the molecule having a disk-shaped substituent, a possibility may arise that the effect of pressure causes alteration in the dihedral angle between a plane of the substituent and that of the benzene ring. We will expand on this point in another paper.

Together with benzene or *p*-xylene as an internal reference compound, 1,4-disubstituted benzenes were mainly used as the sample because of the simplicity of their ring proton spectra. Bromobenzene-*3,5*-d_2 was also employed as an example of *mono*substituted benzene. The proton spectra of the bromobenzene-*3,5*-d_2 consisted of two slightly broadened signals[3] which were readily assigned to the ring protons ortho and para to the bromine substituent. *n*-Hexane was our first choice of the solvent and was used throughout this study. We chose this for two reasons: (i) it does not solidify at high pressure and room temperature; and (ii) as to the solvent effect on the proton chemical shift, only the so-called van der Waals interaction plays the major part and this reduces the factors contributing to the pressure dependence of the chemical shift.

Experimental Section

All the materials were purified finally by fractionation or by recrystallization and identified with their physical constants and proton NMR spectra. *n*-Hexane was purified[4] by shaking it several times with concentrated sulfuric acid, then with a 0.1 N solution of potassium permanganate in 10% sulfuric acid, and finally with a 0.1 N solution of permanganate in 10% sodium hydroxide. It was then washed with water, dried over sodium hydroxide pellets, and fractionally distilled in a 30-cm Widmer fractionating column. The fraction boiling between 66.0 and 68.0 °C was used. Bromobenzene-*3,5*-d_2 was prepared according to the method reported by R. I. Akawie et al.[5] Usually 4 mol % of substituted benzene sample was dissolved in *n*-hexane along with 1 mol % of benzene as an internal reference. Measurements on more dilute solutions, containing 1.8 mol % of substituted benzene and 0.2 mol % of benzene, were also carried out for 1,4'-dibromobenzene and for bromobenzene-*3,5*-d_2 to examine the concentration dependence of the relative pressure shift. No significant change was observed in the relative pressure shift on dilution. Accordingly, the present data based on the 5 mol % solutions may be considered to represent the pressure dependence of the chemical shift for substituted benzenes at infinite dilution in *n*-hexane. When complications arose from the overlapping of the sample and reference signals, *p*-xylene was used as an internal reference. This relative pressure shift was converted to the benzene reference scale by measuring the *p*-xylene relative shift against benzene. The validity of the procedure was confirmed for samples which admit both benzene and *p*-xylene as reference.

The high-pressure equipment was the same as that described in the previous report[1d,e] except for some minor improvements. For example, the design of the PTFE safety jacket to hold the pressure resisting glass cell[1e] was improved to fit the 100-MHz NMR probe. A high-pressure high-resolution NMR experiment was safely conducted on a Jeol PS-100 high-resolution spectrometer operating at 100 MHz and equipped with a standard high-resolution NMR probe and with a variable temperature controller. The continuous wave (CW) operation was used, while the field control was effected by means of the two-sample system (external) NMR lock. Prior to a measurement at a fixed pressure, the temperature was directly read in a thermometer held in a PTFE jacket, which was settled in the NMR probe. Thus the temperature of the sample under the NMR condition was estimated to be maintained at 34.8 ± 0.2 °C throughout the experiment. Relative chemical shifts were determined by means of the linear interpolation between known audio-frequency sidebands, which were calibrated to 0.01 Hz with the aid of a frequency counter. The accuracy for the measured relative chemical shifts was in general ±0.1 Hz and for bromobenzene-*3,5*-d_2 ±0.2 Hz for 10–15 repeated measurements at a fixed pressure of up to 2000 kg cm^{-2}.

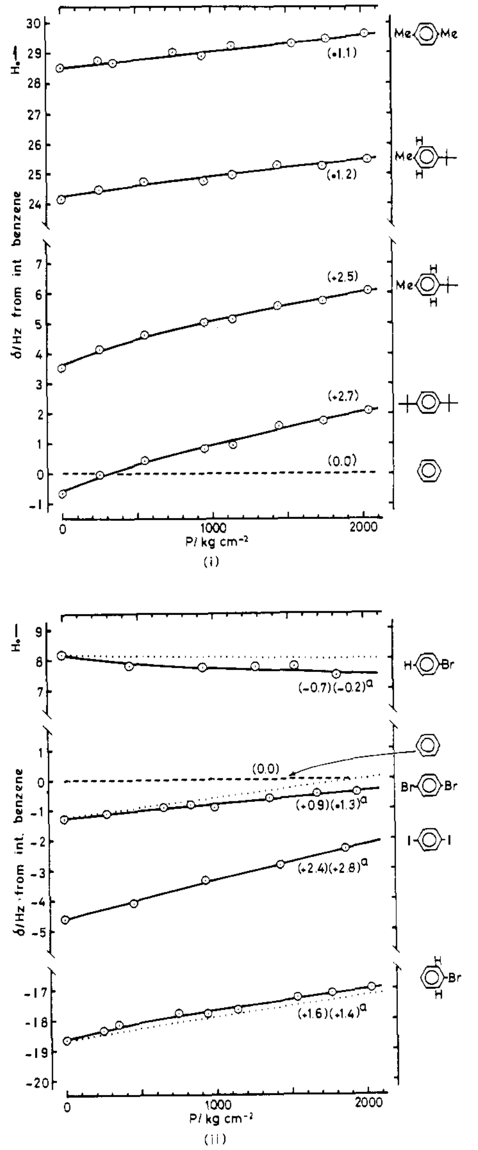

Figure 1. Pressure dependence of the ring proton chemical shifts, δ, of (i) alkylbenzenes and (ii) halobenzenes relative to the internal benzene resonance. The dotted line represents the pressure dependence corrected for the $\Delta\sigma_E(P)$ contribution (see text). Relative pressure shifts $\delta\Delta$, in hertz caused by the compression of the sample up to 2000 kg cm^{-2} are given in parentheses. Relative pressure shifts corrected for the $\Delta\sigma_E(P)$ contribution are noted with a superscript a.

Results and Discussion

The pressure dependence of the ring proton chemical shifts relative to benzene (broken line) as an internal reference is shown in Figure 1. It is important to remember that the reference benzene molecule also feels the effect of pressure and hence, when viewed from the absolute standard, its resonance probably is shifted toward low field with increasing pressure for the reason discussed later. It can be seen from Figure 1 that the ring protons ortho to the substituent show progressive shifts with increasing pressure toward high field relative to the benzene resonance.

Since the pressure effect on the chemical shift arises from the intensified interaction between the resonating proton and medium molecules, the variation of the pressure dependence with substituents can certainly be attributed to the difference

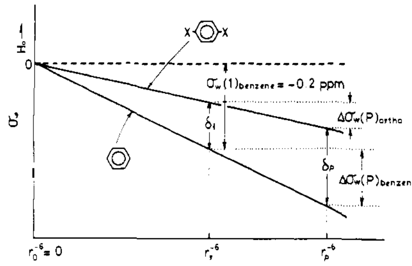

Figure 2. Schematic representation of the dependence of the σ_w contribution on the intermolecular separation r.

in the ability of the substituent to affect the proton-medium interaction. Therefore we shall examine the present observations in terms of the medium effects on the NMR chemical shifts. Generally the medium effects can be divided into five contributions:[6]

$$\sigma_{medium} = \sigma_b + \sigma_a + \sigma_w + \sigma_E + \sigma_H \qquad (1)$$

Under the present experimental conditions employing (a) the internal referencing system and (b) sufficiently dilute solution in nonpolar, magnetically nearly isotropic n-hexane, eq 1 may well be simplified to the form

$$\sigma_{medium} = \sigma_w + \sigma_E \qquad (2)$$

where σ_w denotes the contribution arising from the weak van der Waals interaction between the resonating proton and medium molecules and σ_E represents the effect due to the polarization of the C-H bond caused by the so-called reaction field. Assuming that the compression of the liquid sample exerts influence both on the σ_w and on the σ_E term, the absolute pressure dependence of the chemical shift, Δ, viewed from a fictitious 1-atm reference, which is equivalent to an external 1-atm reference with bulk susceptibility correction, can be described as

$$\Delta = \Delta\sigma_w(P) + \Delta\sigma_E(P) \qquad (3)$$

in which $\Delta\sigma_w(P)$ and $\Delta\sigma_E(P)$ represents a change in the corresponding σ due to compression of the sample from 1 atm to an elevated pressure P. The observed relative pressure shift, $\delta\Delta$, is then expressed in terms of the structural effect (substituent effect) on the $\Delta\sigma_w(P)$ term and the $\Delta\sigma_E(P)$ term.

$$\delta\Delta = [\Delta\sigma_w(P)_{sample} - \Delta\sigma_w(P)_{ref}] + [\Delta\sigma_E(P)_{sample} - \Delta\sigma_E(P)_{ref}] \qquad (4)$$

Figure 1 clearly shows that the observed $\delta\Delta$ for the ortho proton depends largely on the size, and not on the polarity of the substituent; there is a steady rise in the $\delta\Delta$ as the substituent size becomes larger. This suggests strongly that the $\delta\Delta$ should be interpreted in terms of the "steric" part of the substituent effect and therefore be mostly accounted for by the contribution of the $\Delta\sigma_w(P)$ term. While it is not possible at present to make a priori evaluation of the substituent steric effect on the $\Delta\sigma_w(P)$ contribution, further support for this view will come from the calculation of the $\Delta\sigma_E(P)$ contribution, which will be shown to be rather small. For the contribution of σ_w, at the ordinary pressure, an order of the magnitude -0.2 ppm has been estimated for some simple organic molecules from the observed difference between the chemical shift of a gaseous sample and that of the sample dissolved in a nonpolar solvent.[6,7] Since σ_w is approximately proportional to the inversed sixth powers of the intermolecular separation,[7c,8] compression of the liquid sample from the ordinary to the higher pressure should also result in the increased contribution of σ_w, which causes a low-field shift of the resonating proton. The bulky substituent ortho to the proton, however, may interfere partly with the approach of medium molecules to that proton and suppresses the increase of the σ_w contribution at high pressure:[9]

$$|\Delta\sigma_w(P)_{ortho}| < |\Delta\sigma_w(P)_{benzene}| \qquad (5)$$

This results in a progressively increasing difference, with increasing pressure, between $\Delta\sigma_w(P)_{ortho}$ and $\Delta\sigma_w(P)_{benzene}$, giving rise to a positive (high-field) contribution to $\delta\Delta$ for the substituted benzene. This condition may be schematically illustrated in Figure 2, where the contribution of the σ_w term was related to the intermolecular separation in the gaseous state, r_0, at ordinary pressure, r_I, and at high pressure, r_P. For simplicity, linear dependence of the σ_w contribution to r^{-6} was assumed neglecting the correction term for the "site factors".[7c] δ_I and δ_P explains effect of the substituent X on the σ_w contribution at ordinary pressure and at high pressure, respectively.

It can be noted in Figure 1(i) that the ring protons of 4-*tert*-butyltoluene ortho and meta to the methyl group show quite similar pressure dependence to that of p-xylene and of 1,4-di-*tert*-butylbenzene, respectively. This clearly indicates that the size of the meta substituent has no influence on the $\Delta\sigma_w(P)$ contribution and that the steric effect of the meta substituent can well be neglected.

We may now consider contribution of the $\Delta\sigma_E(P)$ term, the magnitude of which may be experimentally evaluated in the case of para proton resonance of bromobenzene-*3,5*-d_2, since the steric effect of the bromine substituent on the para position is sufficiently small and only the $\Delta\sigma_E(P)$ plays a decisive role in contributing to the $\delta\Delta$.

$$\delta\Delta_{para} = [\Delta\sigma_E(P)_{para} - \Delta\sigma_E(P)_{benzene}]$$

We can assume

$$\Delta\sigma_E(P)_{benzene} \simeq 0$$
$$\delta\Delta_{para} \simeq \Delta\sigma_E(P)_{para} \qquad (6)$$

Thus, from Figure 1(ii), we can estimate a $\Delta\sigma_E(2000)$ contribution of -0.7×10^{-2} ppm due to the compression up to 2000 kg cm^{-2} for the para proton of bromobenzene. We might also be able to estimate the magnitude of this contribution by the use of Buckingham's electric field theory.[11] The theory relates σ_E to the reaction field, which can be expressed in terms of the dielectric constant ϵ of the solvent, the dipole moment μ of the solute and the polarizability α of the solute. Assuming that the $\Delta\sigma_E(P)$ mainly arises from a change in ϵ due to the increased density at high pressure and using $\epsilon = 1.880$ and $\epsilon = 2.062$ for n-hexane[12] at atmospheric pressure and at 2000 kg cm^{-2}, respectively, $\Delta\sigma_E(2000)$ for the para proton resonance of bromobenzene with $\mu/\alpha = 1.3 \times 10^5$ is calculated to be -0.5×10^{-2} ppm. The agreement with the experimental value of -0.7×10^{-2} ppm is quite satisfactory and justifies the use of Buckingham's approximation hereafter.

For the ortho proton of bromobenzene, for which the reaction field vector gives a shielding effect, we can calculate $\Delta\sigma_E(2000) = 0.2 \times 10^{-2}$ ppm or 0.2 Hz at $\nu_0 = 100$ MHz, which is 10 ~ 15% of the observed $\delta\Delta$ and is small enough to be masked by the van der Waals term, $\Delta\sigma_w(P)$.

The electric quadrupole moment θ of 1,4-disubstituted benzene also polarizes the surrounding medium and this generates the reaction field. Thus Buckingham, Schaefer, and Schneider[6] have made an estimate $\sigma_E = -0.08$ ppm for 1,4-dinitrobenzene in n-hexane at ordinary pressure. Assuming that θ for 1,4-dibromobenzene and 1,4-diiodobenzene is less than that for 1,4-dinitrobenzene by a factor of 2.5 and the radius of the molecule $r = 3.5$ Å, we can estimate $\Delta\sigma_E(2000) = -0.4 \times 10^{-2}$ ppm for these molecules. This again seems to be overshadowed by the $\Delta\sigma_w(P)$ contribution in the observed positive $\delta\Delta$. For 1,4-diiodobenzene with a larger radius than that for either 1,4-dibromo- or 1,4-dinitrobenzene, a much smaller $\Delta\sigma_E(P)$ contribution is actually expected. In Figure

1(ii), dotted lines for the halobenzenes represent the pressure dependence of ring proton resonance corrected for the $\Delta\sigma_E(P)$ contribution, that is the pressure dependence which might be related exclusively to the steric effect of the substituent ortho to the resonating proton. It can be seen that the dotted line for the ortho proton of bromobenzene-*3,5-d*$_2$ behaves almost identically with that for the ring proton of 1,4-dibromobenzene. This is consistent with the foregoing aspect that the meta substituent does not contribute to the $\Delta\sigma_W(P)$ term and constitutes further support for the validity of present estimations on the $\Delta\sigma_E(P)$ contribution. Since the quadrupole moments of 1,4-dialkylbenzenes and the dipole moment of 4-*tert*-butyltoluene are extremely small, the $\Delta\sigma_E(P)$ contributions in these molecules become even much smaller and may be safely neglected.

We thus arrive at the view that the observed $\delta\Delta$ for the ortho proton is largely accounted for in terms of the contribution of σ_W, which varies depending on the extent of the substituent steric effect to hinder the approach of the medium molecule to the resonating proton. In this respect, the measurement of the $\delta\Delta$ is expected to offer a means of experimentally establishing a measure of the "steric effect" of the ortho substituent, quantitative evaluation of which might otherwise be really difficult.

The present observation of the substituent steric effect on the σ_W contribution at high pressure indicates that a similar effect must basically exist even at the ordinary pressure (δ_l in Figure 2) and suggests that this effect, in studying the ortho substituent effect on the ring proton resonance,[3,13] should be taken into account as an additional factor in the SCS (substituent chemical shift) other than the electronic (polar) as well as the magnetic anisotropy effect of the substituent.[14]

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References and Notes

(1) (a) J. Jonas, *Rev. Sci. Instrum.*, **43**, 643 (1972); (b) H. Yamada, *Chem. Lett.*, 747 (1972); (c) J. Jouanne and J. Heidberg, *J. Magn. Reson.*, 7, 1 (1972); (d) H. Yamada, T. Ishihara, and T. Kinugasa, *J. Am. Chem. Soc.*, **96**, 1935 (1974); (e) H. Yamada, *Rev. Sci. Instrum.*, **45**, 640 (1974); (f) J. Jonas, *Annu. Rev. Phys. Chem.*, **26**, 167–190 (1975).

(2) A detailed review of recent progress in this area is presented by J. Jonas.[1f]

(3) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(4) J. A. Riddick and W. B. Bunger, *Tech. Chem.*, **2**, 594–596 (1970).

(5) R. I. Akawie, J. M. Scarborough, and J. G. Burr, *J. Org. Chem.*, **24**, 946 (1959).

(6) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

(7) (a) A. A. Bothner-By, *J. Mol. Spectrosc.*, **5**, 52 (1960); (b) N. Lumbroso, T. K. Wu, and B. P. Dailey, *J. Phys. Chem.*, **67**, 2469 (1963); (c) F. H. A. Rummens, W. T. Raynes, and H. J. Bernstein, *ibid.*, **72**, 2111 (1968).

(8) W. T. Raynes, A. D. Buckingham, and H. J. Bernstein, *J. Chem. Phys.*, **36**, 3481 (1962).

(9) Wilbur and Jonas have arrived at the similar view in interpreting a smaller pressure dependence of the ^{19}F chemical shift of 2-chloro benzotrifluoride as compared with that of 4-chloro benzotrifluoride.[10]

(10) D. J. Wilbur and J. Jonas, *J. Magn. Reson.*, **10**, 279 (1973).

(11) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(12) F. I. Mopsik, *J. Res. Natl. Bur. Stand., Sect. A*, 71, 287 (1967).

(13) (a) P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961); (b) G. Socrates and M. W. Adlard, *J. Chem. Soc. B*, 733 (1971).

(14) H. Yamada, Y. Tsuno, and Y. Yukawa, *Bull. Chem. Soc. Jpn.*, **43**, 1459 (1970).

Low Resolution Microwave Spectroscopy. 5. Rotational Isomerism of Propargyl Cyanoformate, Propargyl Trifluoroacetate, Propargyl Fluoroformate, and Propargyl Chloroformate[1]

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Abstract: Low resolution microwave spectra of propargyl cyanoformate and propargyl trifluoroacetate each display three *a*-type band series characterized by $B + C$ values of 1935 (3), 2253 (1), and 2142 (1) MHz for propargyl cyanoformate and 1342 (2), 1507 (1), and 1467 (3) MHz for propargyl trifluoroacetate, associated with three conformational forms designated extended, compact, and intermediate. Propargyl fluoroformate and chloroformate display band spectra from two conformational forms with $B + C$ values of 2515 (1) and 3175 (1) MHz for the fluoroformate and 1938 (2) and 2280 (2) (2235 (2), ^{37}Cl) for the chloroformate, designated extended and compact. For each compound the extended species is consistent with a syn-anti [τ_1(OCOC) = 0°, τ_2(COCC) = 180°)] heavy atom planar structure and the compact species with a syn-gauche [τ_1(OCOC) = 0°, τ_2(COCC) ~ 90°)] structure. The intermediate forms of propargyl cyanoformate and trifluoroacetate are both consistent with a gauche-gauche [τ_1(OCOC) ~ 60°, τ_2(COCC) ~ 270°] structure. The extended and compact forms are of nearly equal energy in all cases. The intermediate forms of propargyl cyanoformate and trifluoroacetate are approximately 1–2 kcal/mol higher in energy. These results parallel previous findings for ethyl esters, demonstrating that the potential functions for internal rotation in ethyl and propargyl esters are similar.

Three conformers in ethyl trifluoroacetate, ethyl chloroformate, and ethyl cyanoformate have been observed and characterized using low resolution microwave (LRMW) spectroscopy.[2] The two most stable forms of each ester, designated extended and compact, have the syn-anti [τ_1(OCOC) = 0°, τ_2(COCC) = 180°] and syn-gauche [τ_1 (OCOC) = 0°,