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Carbon-13 Spin–Lattice Relaxation and Molecular Motion of Diphenyl Dichalcogenides

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Abstract: Spin-lattice relaxation times (T_1) were measured and analyzed for Ph_2X_2 type molecules (X = S, Se, Te), to obtain information on the relative order of magnitude of internal motion rates, which are otherwise inaccessible. The calculations were based on the rigid anisotropic as well as on the isotropic with internal rotation model of reorientation. Both the approaches suggested an interpretation of T_1 data in terms of intramolecular motions that contribute to relaxation at a rate increasing in the order S, Se, Te. In particular, the analyses provided evidence that for Ph_2Se_2 and Ph_2Te_2 the internal motion is much faster than in the Ph_2S_2 molecule, where conformational motions about Ph–S bonds occur at a rate that is comparable to that of overall molecular reorientation.

Introduction

The static stereochemistry of diphenyl disulfide and its selenium and tellurium analogues in the solution state has been the object of previous dipole moment and NMR studies.[2-5] Speculation concerning the origin and the temperature effect of the electrical dipole moments of these molecules recently[5] suggested peculiar variable internal flexibility along the series S, Se, Te. No direct and more detailed information, however, can be attained by conventional NMR techniques as to the motional characteristics of these systems.

Carbon-13 spin–lattice relaxation times are becoming an increasingly powerful tool for studies on internal motions as well as overall molecular tumbling characteristics.[6] The quantitative treatment of relaxation data, which is possible in that the majority of ^{13}C nuclei in organic molecules are relaxed by the dipole–dipole mechanism,[6-8] implies in general a fitting procedure with an appropriate relaxation model. Furthermore, the quantitative description of dipolar relaxation becomes complex when the nuclei are part of a group within the molecule that undergoes internal motion and, in particular, when more than one degree of freedom for internal motion is involved. Owing to these difficulties, the molecules investigated in some detail were mostly chosen for methodological demonstration purposes and not for their intrinsic chemical interest. Previous carbon-13 T_1 studies of structurally simple molecules bearing phenyl groups are reported[9-13] in the literature; these

were instrumental in interpreting the relaxation data in terms of overall anisotropic motion.

A detailed study of the spin–lattice relaxation behavior of diphenyl disulfide (Ph_2S_2), diphenyl diselenide (Ph_2Se_2), and diphenyl ditelluride (Ph_2Te_2) is therefore reported here. The determination of relaxation information for these diphenyl dichalcogenides offered, in fact, an opportunity to apply the method to more complex systems and, at the same time, to gain an insight into their dynamic conformational processes. The present study was thus initiated to provide unequivocal evidence for stereochemical nonrigidity of diphenyl dichalcogenides and to ascertain whether information on the relative order of magnitude of internal molecular motion along the series S, Se, Te could be derived from relaxation times.

Experimental Section

The peak assignments and ^{13}C spin–lattice relaxation times of the compounds studied have been reported in a previous work.[14] Experimental conditions and sources of materials have been described therein.

The proton noise-decoupled ^{13}C spectrum of each compound was recorded under nonsaturating conditions and all protonated carbon nuclei signals were found to have equal integral peak areas. This indicates that the relaxation is dipolar and the conditions for motional narrowing are satisfied.

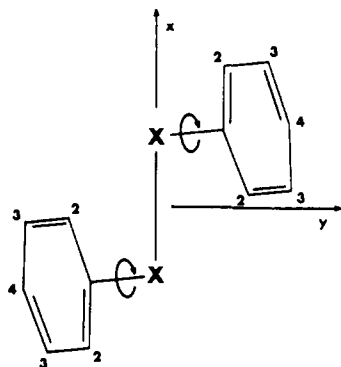All samples were carefully degassed prior to experiments.

Figure 1. The molecular model of a diphenyl dichalcogenide oriented along the coordinate system of axes chosen (the z axis points toward the observer). The numbering scheme adopted reflects the magnetic equivalence observable for the ^{13}C resonances of Ph rings.

The measured ^{13}C spin–lattice relaxation times of diphenyl dichalcogenides under study appear in Table I.

Theory and Computational Methods

Internal rotation superimposed on the overall motion can be expressed in the stochastic rotational diffusion model by means of the general Woessner's equation[15]

$$T_1^{-1} = H[J_1(\omega_0) + J_2(2\omega_0)] \simeq (\tfrac{3}{4})\hbar^2\gamma_C{}^2\gamma_H{}^2 r_{C-H}{}^{-6}$$

$$\times \left[\frac{B_{A1}}{6R_2} + \frac{B_{A2}}{6R_2 + D} + \frac{B_{A3}}{6R_2 + 4D} + \frac{B_{B1}}{R_1 + 5R_2} \right.$$

$$+ \frac{B_{B2}}{R_1 + 5R_2 + D} + \frac{B_{B3}}{R_1 + 5R_2 + 4D} + \frac{B_{C1}}{4R_1 + 2R_2}$$

$$\left. + \frac{B_{C2}}{4R_1 + 2R_2 + D} + \frac{B_{C3}}{4R_1 + 2R_2 + 4D} \right] \quad (1)$$

where $B_{A1} = (\tfrac{1}{8})(1 - 3\cos^2\alpha)^2(1 - 3\cos^2\Delta)^2$; $B_{A2} = (\tfrac{9}{16})$ $\sin^2 2\alpha \sin^2 2\Delta$; $B_{A3} = (\tfrac{9}{16})\sin^4\Delta \sin^4\alpha$; $B_{B1} = (\tfrac{3}{8})\sin^2 2\alpha(3$ $\cos^2\Delta - 1)^2$; $B_{B2} = (\tfrac{3}{4})(\cos^2 2\alpha + \cos^2\alpha)\sin^2 2\Delta$; $B_{B3} =$ $(\tfrac{3}{4})[\sin^2\alpha + (\tfrac{1}{4})\sin^2 2\alpha]\sin^4\Delta$; $B_{C1} = (\tfrac{3}{8})\sin^4\alpha(3\cos^2\Delta$ $- 1)^2$; $B_{C2} = (\tfrac{3}{4})[\sin^2\alpha + (\tfrac{1}{4})\sin^2 2\alpha]\sin^2 2\Delta$; $B_{C3} = (\tfrac{3}{16})[(1$ $+ \cos^2\alpha)^2 + 4\cos^2\alpha]\sin^4\Delta$. In this equation R_1 and R_2 are the rotational-diffusion constants of the ellipsoid about its major and minor axis, respectively; D is the rotational-diffusion constant of the rotating group with respect to the axis of the ellipsoid. The angle made by the axis of internal motion and the principal symmetry axis of the ellipsoid is given by α, whereas Δ is the angle between the pertinent C–H bond and the axis of internal rotation. The remaining symbols have their usual meaning as in ref 15.

The moments of inertia for each molecule under study were calculated from the pertinent x-ray crystallographic data.[16-18] The direction of the principal axis system of the moment of inertia tensor with respect to the system of axes shown in Figure 1 is given by the direction cosines reported in Table II. The corresponding tensors of inertia from which the direction cosines were calculated are given in the same table together with the principal axes of moment of inertia tensors. These quoted figures indicate that all molecules treated can be reasonably approximated to an axially symmetric model, I_B and I_C values being comparable among them and largely different from I_A. In order to apply eq 1 the overall motion was assumed independent of internal modes and vice versa. This assumption is justified because the moment of inertia tensors were seen to vary by a small amount when considering models with different rotational angles about Ph–X bonds. In each case, however, values of three rotational-diffusion constants cannot be directly obtained from the T_1 set of values for a single molecule. Therefore, to assist in the interpretation of the measured relaxation times we assumed for our initial calculations a rigid

Table I. ^{13}C Spin-Lattice Relaxation Times $(T_1)^{a,b}$ for Diphenyl Dichalcogenides Ph_2X_2 in $CDCl_3$ Solution

| X | T_1, s^c | | |
	C-2	C-3	C-4
S	6.4	6.4	5.0
Se	6.8	6.8	3.7
Te	5.7	5.7	2.8

^{a} Determined at 25.2 MHz and 38 °C. ^{b} The T_1 of the quaternary carbon (C-1) was measured to be 50.0 s for all molecules. ^{c} Estimated accuracy of the observed T_1 values is better than ±5%.

anisotropic model which corresponds to the skew conformation established for each molecule in the solid state.[16-18] Under this assumption, the internal motion diffusion constant D vanishes and eq 1 becomes simplified. In principle, it should be stressed that the rotational-diffusion constants depend on the molecular friction constant ($\beta = 8\pi r^3\eta$ for a sphere of radius r) and thus primarily on the shape of the molecule. However, for the adopted rigid model the molecular shape and geometries can be reasonably assumed, with good approximation, to be unchanged along the series, as deducible by inspection of corresponding x-ray crystal data. On this basis, for the above model, the ratios between T_1 values for C-2, C-3, and C-4 atoms in each molecule should not vary on passing from X = S to X = Se and X = Te. Actually, these experimental ratios are strongly dependent on the X atom; it was necessary, as a consequence, in order to retain the original rigid model, to make the different assumption of some relation between the rotational diffusion coefficients and the moments of inertia. A simple choice appeared to assume that there is proportionality between the rotational-diffusion constants (R_1, R_2) about each of the principal axes and the inverse moments of inertia about these same axes.[19] In this way, the ratio between measured T_1 values for different carbons in the same molecule may thus provide a basis for a comparison with the corresponding calculated ratio under the assumption of anisotropic rigid overall motion and *no internal rotation*. Results of these computations, that are essentially *heuristic*, are shown in Table III.

An *alternative* estimate of the motional characteristics of Ph_2X_2 systems can be made on the basis of relaxation data by assuming overall isotropic tumbling and internal fast rotation of the phenyl groups about Ph–X bonds. If internal rotation is assumed to be diffusional, the correlation time τ_c is given by the appropriately modified[20] Woessner's equation:

$$\tau_c = (\tfrac{3}{4}) \sin^4\Delta (6R_{iso} + 4D)^{-1} + 3\sin^2\Delta\cos^2\Delta$$
$$\times (6R_{iso} + D)^{-1} + [(\tfrac{1}{2})(3\cos^2\Delta - 1)]^2(6R_{iso})^{-1} \quad (2)$$

that, for the C-4 atom, is simplified to

$$\tau_c = \tfrac{1}{6}R_{iso} \quad (3)$$

In these equations R_{iso} is the isotropic rotational-diffusion constant ($R_{iso} = R_1 = R_2$), whereas the symbols Δ and D have the meaning indicated previously. The correlation time τ_c is related to T_1 by

$$T_1^{-1} = H\tau_c \quad (4)$$

where the factor H is $(\tfrac{3}{2})\hbar^2\gamma_C{}^2\gamma_H{}^2 r_{C-H}{}^{-6}$. The R_{iso} value for each dichalcogenide examined was obtained from T_1 data for C-4 by means of eq 3, whereas the D/R_{iso} ratio was estimated using eq 2 in combination with the measured T_1s for C-2 and C-3. By this procedure the experimental relaxation times were utilized for comparing the magnitude of the two rotational-diffusion constants and therefore for determining the relative rates of the internal and overall motional processes that occur in each Ph_2X_2 type molecule. Results of the computations are shown in Table IV.

Table II. Calculated Directional Cosines, Tensors of Inertia,[a] and Principal Moments of Inertia[b] (amu Å^2) for Ph_2X_2 Molecules

X	Cos α	Cos β	Cos γ	J_{xx}	J_{yy}	J_{xy}	I_A	I_B	I_C
S	0.34	−0.88	0.34	1501.5	730.8	−422.4	404.4	1505.6	1823.9
Se	0.33	−0.88	0.33	1811.5	908.0	−459.4	564.9	1827.8	2138.3
Te	0.27	−0.92	0.27	2118.1	901.5	−423.1	651.2	2154.3	2332.3

[a] $J_{xx} = J_{zz}$; $J_{xy} = J_{xz} = J_{yz}$. [b] I_A is the moment of inertia relative to the direction of the axis of inertia given by the corresponding directional cosines; I_B and I_C are orthogonal to I_A.

Table III. Calculated[a] and Observed C-2/C-4 and C-3/C-4 Relaxation Time Ratios for Ph_2X_2 Systems

	Calcd		Obsd
X	$T_1(C\text{-}2)/$ $T_1(C\text{-}4)$	$T_1(C\text{-}3)/$ $T_1(C\text{-}4)$	$T_1(C\text{-}2),(C\text{-}3)/(C\text{-}4)$
S	0.77	0.83	1.28
Se	0.74	0.86	1.84
Te	0.60	0.85	2.04

[a] Rigid anisotropic model assumed.

Table IV. Values of Overall (R_{iso}) and Internal Diffusion (D) Coefficients[a] for Isotropic Molecular Motion of Ph_2X_2 Systems

X	D^{-1}, s × 10^{-9}	R_{iso}^{-1}, s × 10^{-9}	D/R_{iso}
S	2.56	2.12	0.83
Se	1.65	2.87	1.74
Te	1.74	3.79	2.18

[a] Calculated from experimental relaxation data.

Discussion

Before discussing results of the analyses, it is interesting to note that for each compound examined the measured T_1 values for C-2 and C-3 atoms are equal within the limit of the standard experimental error. This indicates that the approximate symmetry axis of the Ph_2X_2 molecule and the Ph–X axes intersect each other and are nearly perpendicular. Since the symmetry axis coincides with the principal axis of inertia that was calculated assuming for the molecule the skew conformation established in the solid state, the observed equality of the relaxation times measured for C-2 and C-3 suggests that this conformation is retained in the solution state.

The calculated values of the C-2/C-4 and C-3/C-4 relaxation time ratios are rather smaller than those observed (Table III). On this basis the model of overall anisotropic reorientation of a rigid body as well as the occurrence of rigidly fixed conformations for diphenyl dichalcogenides can be probably ruled out. It could be, however, objected that a simple comparison between calculated and experimental relaxation time ratios C-2/C-4 and C-3/C-4, which are small and subjected to a large error, is a somewhat approximate criterion for deciding whether reorientation is best described by the anisotropic model. Accordingly, we next used eq 1 to obtain the fitting R_1/R_2 ratio from the experimental T_1 values. The procedure provided a reasonable R_1/R_2 value (0.38) for Ph_2S_2, whereas no physically meaningful roots were obtained for Ph_2Se_2 and Ph_2Te_2. This indicates that, even though no optimal fits of relaxation time ratios are produced by the anisotropic model, this is liable to provide acceptable conclusions for the Ph_2S_2 molecule. It must be furthermore concluded that anisotropic overall tumbling is to be definitely excluded as the dominant reorientational mechanism in the case of Ph_2Se_2 and Ph_2Te_2 molecules, where internal motions can be therefore considered much faster than in the Ph_2S_2 system. It is now worth mentioning that dielectric relaxation time data for Ph_2S_2[21] suggested a rigid conformation about the S–S bond; the difference presently found between calculated and experimental spin-lattice relaxation time ratios in this molecule thus appears reasonably attributable to the internal motions that can occur about Ph–S bonds at a rate which does not affect the overall tumbling. This finding agrees fairly well with previously reported conclusions based on theoretical MO calculations and ^{1}H NMR experiments.[4] A similar conclusion cannot be drawn in the case of Ph_2Se_2 and Ph_2Te_2, since additional conformational flexibility about the X–X bond can be predicted on the basis of dipole moment measurements[5] for these systems. It

is clear, in fact, that with enhanced flexibility in the molecular system multiple internal motions contribute to the reorientation process much more than overall molecular motions and thus the simple approximation of a rigid anisotropic model used here does not work so well.

Table IV contains the results of the further analyses that were made on the assumption that molecules behave isotropically and Ph–X bonds rotate rapidly. This procedure seemed, in principle, more useful to assess in some quantitative way the degree of conformational mobility along the series of diphenyl dichalcogenides under study. Data in Table IV, in fact, reveal a definite trend in the values of the ratio between the internal and overall rotational-diffusion constants, that can be reasonably accounted for in terms of an increasing internal motional rate for Ph_2X_2 type molecules in the order X = S ≫ X = Se > X = Te. In particular, in the case of X = S the near equality of D and R_{iso} indicates that internal motions about Ph–S bonds occur at a rate comparable to that of the overall isotropic tumbling. The structure of this molecule can be thus considered as a quasi-rigid one with respect to those of Ph_2Se_2 and Ph_2Te_2 where the D constants considerably overcome R_{iso} and, accordingly, provide evidence for internal motions that contribute to relaxation at a rate that is greater for the Ph_2Te_2 molecule.

In conclusion, these studies have shown that, even if interpretation of T_1 data on diphenyl dichalcogenides can be made assuming anisotropic overall motion of a rigid body, the use of the model of an isotropically reorienting body that undergoes internal motion provides further complementary results that are in some quantitative agreement with the trends in the measured relaxation data. However, our purpose in presenting the above analyses was not to promote any particular model, but rather to indicate that relaxation rates are valuable in elucidating the intramolecular motion characteristics of unusual systems such as diphenyl dichalcogenides. It was also gratifying to observe that the T_1 data conclusions presented here, which offer conformational informations on a time scale of 10^{11} s^{-1}, agree satisfactorily with previous findings based on the use of more conventional techniques (dipole moment data). These suggested[5] that some rotational constraint occurs for Ph_2S_2 about Ph–S bonds, but that increasingly less hindered rotation is attained on passing to the analogues (Se and Te compounds).

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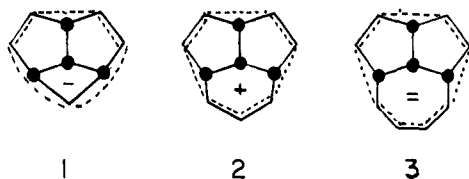
Photoelectron Spectra and Orbital Interactions in Methylenenortriquinacenes

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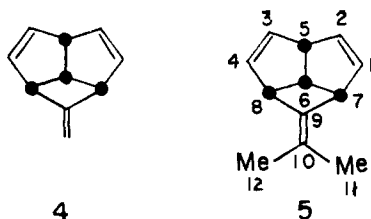
Abstract: Analysis of the photoelectron spectra of nortriquinacene (**6**), 2-methylenenortriquinacene (**4**), 2-isopropylidenenortriquinacene (**5**), and their tetrahydro derivatives has confirmed that the exocyclic double bond does not interact with the endocyclic π bonds. Additionally, it has been possible to demonstrate that the order of the latter orbitals is normal (A over S), in agreement with ab initio STO-3G calculations, but not with MINDO/2 and -3 calculations. These findings agree well with existing chemical and spectroscopic evidence as to the lack of homoaromaticity in these compounds and analogous trishomocyclopentadienides.

Recently, Paquette and co-workers successfully synthesized several precursors to the trishomocyclocyclopentadienide anion **1**, but found no evidence for homoaromaticity in these

systems.[5] Similarly, attempts to generate the trishomotropylium ion **2**[6] and trishomocyclooctatraenide dianion **3**[7] showed homoaromatic stabilization to be lacking in these species. Calculations are also in agreement with the absence of significant conjugation in such systems. For example, **1** is predicted by MINDO/3 to have a pyramidal rather than trigonal anionic carbon.[5] Furthermore, exomethylene derivatives of nortriquinacene show no chemical or ^{13}C spectroscopic evidence for homoconjugative interaction.[5]

We have now used a sensitive probe of orbital interactions, photoelectron (PE) spectroscopy, as well as ab initio molecular orbital (MO) calculations, to investigate the orbital interactions present, or absent, in the methylenenortriquinacenes **4**

and **5**. In particular, the main question to be answered in this study was whether the apparent lack of interaction in these systems is due only to poor overlap of component π orbitals with each other, or whether some combination of conjugative (through-space) and hyperconjugative (through-bond) interactions present in the particular carbon skeletons studied cancels stabilizing interactions which might otherwise take place.

Photoelectron Investigations of π Ionizations. Photoelectron spectroscopy is a sensitive probe of interaction between π systems. For example, three ethylenic π orbitals unite in the benzene molecule to form the familiar degenerate HOMOs and a lower energy π orbital; the PE spectrum shows that there is a 3-eV difference between the energies required to remove electrons from these two types of orbitals. Thus, ionization potentials (IPs) of 9.24 and 12.3 eV are observed in the benzene molecule,[8] and these can be equated to the negatives of the orbital energies of the molecule, using Koopmans' theorem.[9] Using a linear combination of bonding orbitals (LCBO) model in which three isolated π orbitals interact to form the orbitals of benzene, and neglecting overlap, the 3-eV split translates into a resonance integral of 1 eV resulting from π interactions of ethylene units separated by 1.397 Å.

In 1,4,7-cyclononatriene (trishomobenzene), a 0.9-eV split between the degenerate highest occupied molecular orbitals (HOMOs) and the lowest π orbital[10] indicates a resonance integral of 0.3 eV, resulting from the mixed σ and π interactions of ethylenic units separated by 2.46 Å.[11] In triquinacene (a trishomobenzene), a split of only 0.35–0.4 eV[12] leads to a lower limit of 0.1 eV for the resonance integral between the π orbitals of ethylene units separated by 2.533 Å.[13] This is a lower limit, since hyperconjugative interactions are believed to destabilize the lowest π orbital in this molecule,[12] making