interactions, but not to the secondary structure. It is important to investigate the displacements of the ^{15}N chemical shift tensors of the ^{15}N-labeled glycine residue (Gly*) in a series of copolypeptides $[\text{Ala},\text{Gly}^*]_n$ as compared with those of Ala* residue in $[\text{Ala}^*,\text{Gly}]_n$, which will be published in the following paper.[36]

Conclusion

It was demonstrated that the isotropic ^{15}N chemical shift (σ_{iso}) is sensitive to the primary, secondary, and higher ordered structures of polypeptides in the solid state. It was found to be profitable to determine the main-chain conformation of homopolypeptides and copolypeptides with identical primary structure (amino acid sequence) on the basis of the conformation-dependent σ_{iso}. Thus, this method may be applicable to investigation of conformational changes in natural proteins with identical primary structures in the solid state. However, it may generally be difficult to estimate the main-chain conformation of a variety of copolypeptides and natural proteins on the basis of σ_{iso}. For such polypeptides, on the other hand, we showed that the ^{15}N chemical shift tensors (σ_{11}, σ_{22}, σ_{33}) give information on the structures of polypeptides rather than σ_{iso}, using a series of ^{15}N-labeled copolypeptides $[\text{Ala}^*,\text{X}]_n$. In particular, we have confirmed that σ_{22} is governed mainly by secondary structures (the right-handed or left-handed α-helix and the β-sheet form) rather than by the amino acid sequences of polypeptides. The σ_{22} of the Ala* residues in the copolypeptide with the α-helix form was separated from that of the β-sheet form. Therefore, it is now possible to determine the main-chain conformation of copolypeptides (or probably of natural proteins) on the basis of σ_{22}, if the ^{15}N-labeled copolypeptide or natural protein can be provided. Furthermore, the chemical shift tensors other than σ_{22} of the Ala* residue seem to be closely related not only to the secondary structure but also to the primary and higher ordered structures of copolypeptides. However, the correlation between these structures and the ^{15}N chemical shift tensors is not clarified at present, and therefore, a further study is needed.

Supplementary Material Available: Synthetic conditions of some ^{15}N-labeled polypeptides $[\text{Ala}^*,\text{X}]_n$ (Table I) and conformational characterization of solid polypeptides determined by the ^{13}C CP-MAS NMR, IR, and far-IR methods (Table II) (2 pages). Ordering information is given on any current masthead page.

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Low-Temperature NMR Study of Conformational Equilibration and Reversible Covalent Association in Dithioacetic Acid

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Contribution from the Department of Chemistry, Jackson State University, Jackson, Mississippi 39217. *Received November 2, 1989*

Abstract: The proton NMR spectrum of a dilute solution (0.2%) of dithioacetic acid at −106 °C in CD_2Cl_2 shows separate methyl and SH signals for the *E* and *Z* conformations, with the *Z* isomer favored by 0.12 kcal/mol. The free energy barriers at −89 °C are 8.8_5 and 8.9_7 kcal/mol. For the neat liquid or more concentrated solutions in several solvents, the compound is appreciably associated, with the amount of monomer depending upon concentration, temperature, and solvent. At 19.5 °C, the carbon peaks of neat dithioacetic acid are accounted for by monomer (61%), dimer (38%), and a small amount of cyclic trimer (ca. 1%). Spectra taken at lower temperatures in suitable solvents show that the dimer exists in two forms; the free-energy barriers for interconversion of the two forms are 8.7_6 and 8.7_7 kcal/mol.

Dithiocarboxylic acids have been known for over 100 years,[1,2] and several physical studies of members of this class have been reported.[2] Dithioformic acid is monomeric in the gas phase[3,4,5] and was found in a microwave study[3,4] to exist as a mixture of *E* and *Z* conformations, with the *Z* favored by 1.0 kcal/mol. An IR study[5] and molecular orbital calculations[5,6,7] also show that the *Z* conformation is lower in energy. The compound has been reported[8,9] to exist in the condensed phase as a cyclic trimer or polymer.[10]

The higher dithio acids have generally been assumed to be monomeric, except for possible association through hydrogen bonding.[2] The IR spectrum[11] of dithioisobutyric acid showed absorption at 2502 cm^{-1} as the neat liquid and at 2566 cm^{-1} in dilute (1.5%) solution in CCl_4; both peaks were observed at intermediate concentrations and were attributed to S–H stretching in hydrogen-bonded dimer and monomer, respectively. Because the thiocarbonyl absorption remained constant at about 1220 cm^{-1} for several concentrations in carbon disulfide, the dimerization was assumed to be of the type S–H···S(–H) and not S–H···S(=C). The position of the SH peak in the NMR spectrum shifts slightly upfield upon dilution in CCl_4 (δ 6.40 for the neat liquid to 6.02 for a 1.5% solution), and this shift also was taken[11] to be evidence for a monomer–dimer equilibrium of this type. The dipole moment for dithioisobutyric acid (2.13 D in benzene at 20 °C) was interpreted[11] as evidence for the *Z* conformation in this solution.

The room temperature proton NMR spectrum of trifluorodithioacetic acid was reported[12] to show a complex group of signals consisting of five peaks centered at δ 2.65, whose intensities after deuteration greatly decreased. The authors did not discuss possible reasons for the large number of peaks and interpreted the NMR spectrum,[12] mass spectrum,[12] and IR spectrum[12,13] in terms of the monomer, although later studies[11,14] give chemical shifts of δ 6.0

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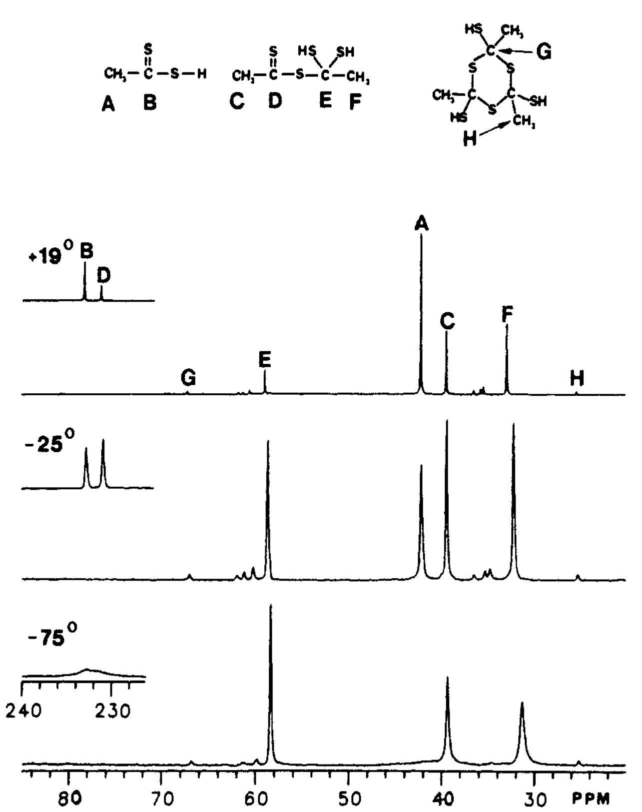

Figure 1. Carbon-13 NMR spectra (75.57 MHz) taken at several temperatures for neat dithioacetic acid.

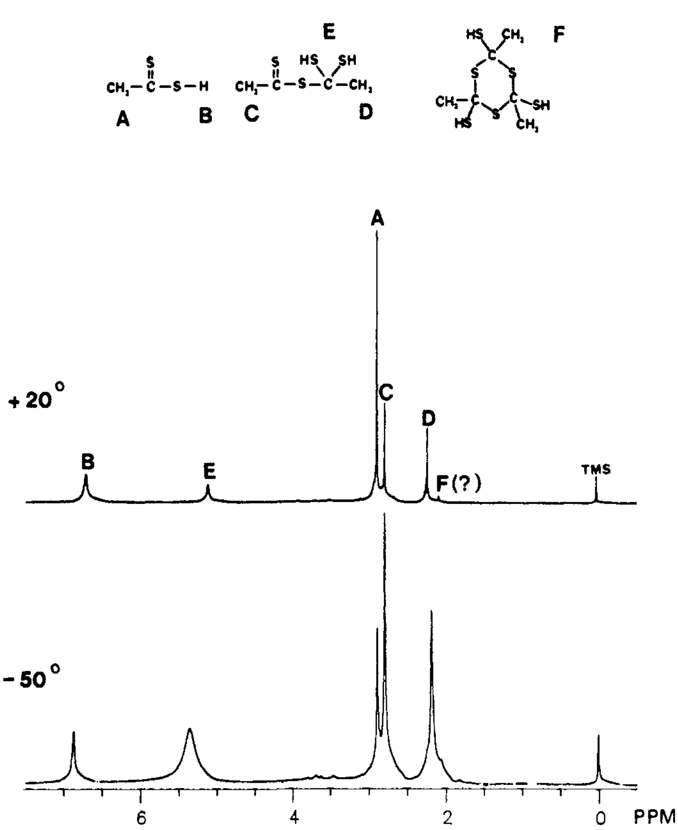

Figure 2. Proton NMR spectra (300 MHz) taken at two temperatures for neat dithioacetic acid.

to 6.5 for the SH protons of dithio acids. Vibrational spectra for dithiobenzoic acid have also been reported.[15]

Proton NMR chemical shifts of δ 2.85 and 6.5 were recorded[14] for dithioacetic acid (**1**), and the IR spectrum was studied[16] for both the liquid and gas phases. Fausto et al.[7] carried out ab initio SCF-MO calculations for **1** and estimated that the *Z* conformation is more stable than the *E* by 1.92 kcal/mol (STO-3G) or 2.00 kcal/mol (3-21G). Also calculated were the dipole moments for the two conformations and the barriers for their interconversion.

We report here an experimental determination of the rotational barriers in dithioacetic acid and show that extensive reversible, covalent association occurs in the neat liquid and in concentrated solutions.

Experimental Section

Dithioacetic acid was prepared by treatment of carbon disulfide with methylmagnesium bromide, followed by addition of dilute hydrochloric acid, using a procedure similar to the one described by Beiner and Thuillier.[14] The compound was purified by distillation, bp 39 °C at ca. 20 mm (lit.[14] bp 31–32 °C at 13 mm).

Proton and carbon NMR spectra were taken on a General Electric GN-300 wide-bore spectrometer operating at 300 MHz for protons and 75.57 MHz for carbon. The spectrometer was unlocked, except for those samples that contained deuterated solvents (dichloromethane-d_2 or toluene-d_8). Proton spectra were taken with a 51° flip angle, 3 s delay between pulses, and a sweep width of ±3000 Hz (quadrature phase detection), except where noted. The flip angle, delay time, and sweep width were 135°, 15 s, and ±15 000 Hz for the carbon spectra of Figure 1, and 108°, 3 s, and ±25 000 Hz for the remaining spectra, except where otherwise noted; the block size was 32K, with one exception described below. The use of a flip angle of greater than 90° for the carbon spectra was unintentional. The conditions used for the ^{13}C spectra (large flip angle, short delay time, low digital resolution, and continuous broadband decoupling) limit the usefulness of these spectra for quantitative studies, and spectra were retaken under more favorable conditions for the neat compound (carbon NMR) and for a dilute solution at –90 °C (proton NMR), as described below.

Temperatures were measured by replacing the sample with an NMR tube containing solvent and a copper–constantan thermocouple, except for the proton spectra of Figure 2.[17] In an earlier DNMR study of phenyl formate,[18] we found that the coalescence temperature for the ipso carbon of the ring did not change observably when the decoupler was turned off, indicating that the decoupler can be turned off for the thermocouple emf measurements without altering the temperatures.

Spectra were taken with a 5-mm probe, and the signal-to-noise ratios of the carbon spectra were improved by exponential multiplication of the FID, resulting in a line broadening of 3 Hz. Populations at slow exchange were determined by electronic integration, and the populations at coalescence were calculated with the assumption that ΔG° is independent of temperature. Rate constants at coalescence were determined by comparison of the experimental spectra with calculated line shapes,[19] and the corresponding barriers were obtained from the Eyring equation.

Results and Discussion

^{13}C spectra of neat **1** at several temperatures are shown in Figure 1. At +19 °C, six major peaks are observed[20] (δ 232.81, 230.97, 58.80, 42.06, 39.32, and 32.84); those at δ 42.06 and 232.81 decrease in intensity as the temperature is lowered and are assigned to monomeric[21] **1**. The chemical shifts of the re-

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[20] The six small peaks at δ 61.6, 61.1, 60.4, 36.4, 35.6, and 35.3 were found to increase after several months and are assumed to arise from irreversible reaction of **1**. The structure(s) of the compound(s) responsible for these peaks are not certain at this time. G. Levesque et al. have isolated tetramethylhexathiaadamantane and a mixture of two isomers of **3**, which separated from dithioacetic acid after the compound was stored for several weeks in the refrigerator: Levesque, G.; Mahjoub, A.; Thuillier, A. *Tetrahedron Lett.* **1978**, 3847. The cyclic trimers **3** were found to give back the monomer on chromatography or distillation. Proton chemical shifts for the three compounds are given by these authors, and carbon shifts of δ 29.2 and 58.5 have been reported for the tetramethylhexathiaadamantane: Mikolajczyk, M.; Kielbasinski, P.; Barlow, J. H.; Russell, D. R. *J. Org. Chem.* **1977**, *42*, 2345.

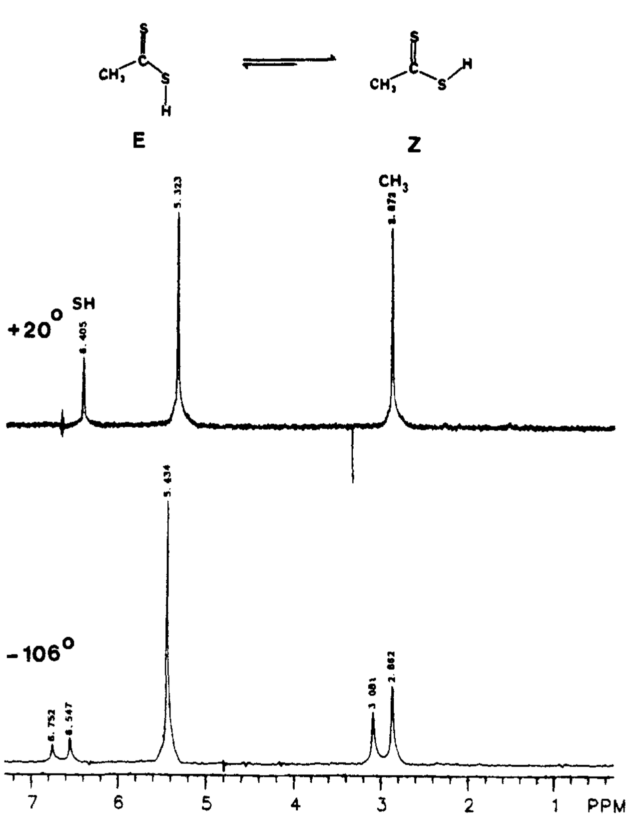
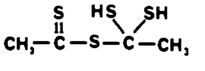


Figure 3. Proton NMR spectra (300 MHz) for a 0.2% solution of dithioacetic acid in CD_2Cl_2, taken at (a) +20 and (b) −106 °C.

maining four peaks are consistent with the structure of the dimer **2**.[22] Peaks at δ 25.32 and 67.09 are assigned to the cyclic trimer **3**, and from the ratio of peak areas (δ 42.06, monomer; δ 39.32



$$\mathrm{CH_3{-}\overset{S}{\overset{\|}{C}}{-}S{-}\overset{HS\ \ SH}{C}{-}CH_3}$$

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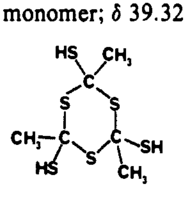

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and 32.84, dimer; δ 25.32, trimer), the percentages by weight of monomer, dimer, and cyclic trimer were calculated to be 55%, 44%,and ca. 1%, respectively. Integration of a spectrum taken at 19.5 °C with a block size of 64K, 45° flip angle, 30 s delay time between pulses, ±15 000 Hz sweep width, and the decoupler off except during acquisition gave corresponding values of 61%, 38%, and 1%. The proton NMR spectrum of the neat liquid at +20 °C shows peaks at δ 2.84 and 6.66 for monomer and 2.19, 2.74, and 5.07 for dimer. The proton spectra at lower temperatures also show large decreases in the monomer/dimer ratios (Figure 2).

Dithioacetic acid in dilute solution (0.2%) in CD_2Cl_2 was found to be largely monomeric, even at low temperatures, and this solution was used to obtain the populations and rotational barriers. The 300-MHz spectrum of **1** at +20 °C shows absorption at δ 2.87 and 6.40 (Figure 3a). At lower temperatures, each signal broadens and splits into two lines of unequal intensity, resulting in chemical shifts at −106 °C of δ 2.86 and 3.08 for CH_3 and 6.54 and 6.75 for SH (Figure 3b). From integration of the methyl signals, populations of 0.41 and 0.59 were obtained,[23] corresponding to a free energy difference of 0.12 kcal/mol, and the major (upfield) conformation is probably *Z*.[24] Populations of 0.42 and 0.58 were estimated at coalescence (−89 °C) with the assumption that $\Delta G°$ is independent of temperature. Rate constants of 118 and 85 s^{-1} were obtained for the $E \rightarrow Z$ and $Z \rightarrow E$ conversions, corresponding to free energy barriers of 8.8_5 and 8.9_7 kcal/mol. The coalescence temperature did not change observably when the concentration was increased to 1%, and this suggests that interconversion of conformations occurs by rotation, rather than by intermolecular exchange of the acidic proton.

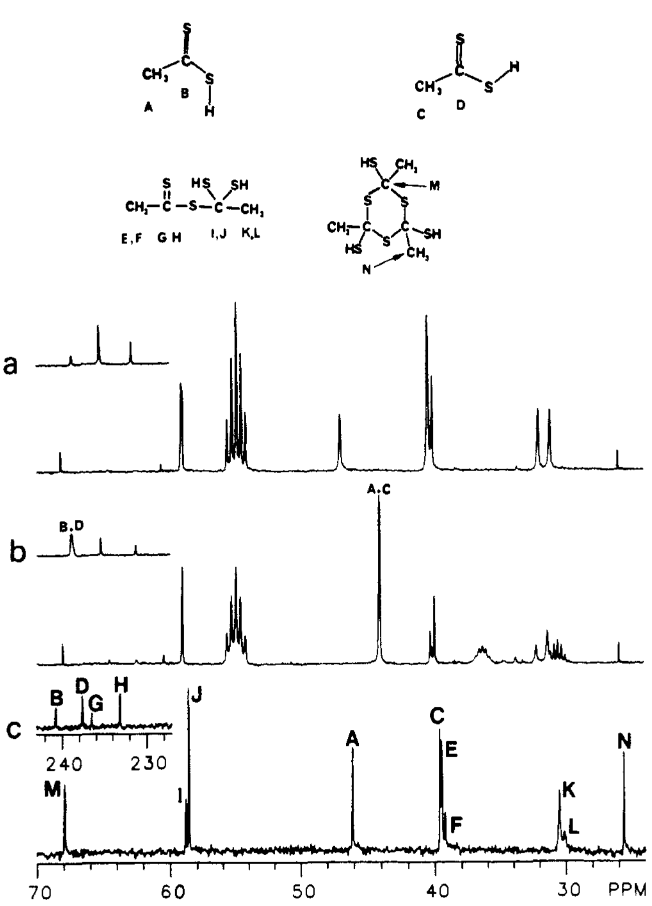

Figure 4. Carbon-13 NMR spectra (75.57 MHz) of 25% solutions of dithioacetic acid in several solvents: (a) −105 °C, solvent CD_2Cl_2; (b) −110 °C, solvent 3:1 by volume of CD_2Cl_2 and DMF-d_7; (c) −140 °C, solvent 1:3:1 by volume of CHF_3, $CHClF_2$, and $CHCl_2F$. The peak assignments for C and E may be reversed.

Decoalescence of all four carbon signals of the dimer was observed at low temperatures in more concentrated solutions (Figure 4). In spectra a and c in Figure 4, both the monomer and dimer are at slow exchange, but in the more polar solvent used for spectrum b, the monomer is exchanging rapidly. The two dimer peaks near δ 40 are partially obscured by the upfield monomer peak in spectrum a, but these peaks can be clearly seen in the second and third spectra. The two sets of dimer peaks are nearly equal in intensity for spectrum a of Figure 4, and populations from integration of the peaks at δ 31.93 and 31.05 were estimated to be 0.5_1 and 0.4_9 at −105 °C. These signals coalesce at −90 °C, and free energy barriers for exchange of 8.7_6 and 8.7_7 kcal/mol were calculated. Changing the concentration of **1** from

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[21] "Monomeric" is used to indicate lack of covalent association. The compound may be hydrogen bonded.

[22] As expected, the coupled spectra indicate that the carbons absorbing above δ 45 have three directly bonded hydrogens, and those absorbing below δ 45 have none.

[23] The same populations were obtained with a 45° flip angle, 30 s delay time, sweep width of ±3000 Hz, and block size of 32 K.

[24] The carbonyl carbons of the *E* conformations of alkyl and aryl formates absorb downfield of the corresponding carbons of the *Z* conformations,[18] and a ^{13}C spectrum of 5% **1** in CD_2Cl_2 at −101 °C shows peaks for the thiocarbonyl carbons at δ 238.83 (minor) and 235.56 (major). The changes in populations that occurred with changes in solvent were comparable to the experimental uncertainties; the following populations of the *E* isomer (downfield methyl peaks) were found by proton NMR for 0.2% solutions in the indicated solvents: CD_2Cl_2, −106 °C, 0.41; 1:3:1 CHF_3, $CHClF_2$, $CHCl_2F$, −134 °C, 0.45. A population of 0.43 was found by ^{13}C NMR for a 5% solution of **1** in toluene-d_8 at −107 °C. We have also assigned the major (upfield) thiocarbonyl peak of phenyl dithioacetate to the *Z* conformation.[25]

25% to 15% or 40% gave coalescence temperatures of −90 and −85 °C, respectively, indicating that the process is intramolecular, and the populations for the different concentrations also did not change appreciably. *E–Z* isomerism of the dimer could account for the doubling of peaks, but we have been unable to observe decoalescence for ethyl dithioacetate,[25] and a large population of the *E* isomer was not expected for the dimer. Also, the sensitivity of the two populations to solvent changes is unlike the behavior of **1** or phenyl dithioacetate,[25] which were found to have populations that changed only by small amounts in the several solvents tried. Rotation about the other three carbon–sulfur bonds can occur, but the experimental barriers seem high for these processes.

From integration of spectrum c of Figure 4, the percentages of monomer, dimer, and cyclic trimer were determined to be 35%, 52%, and 13%.

The barriers for monomeric dithioacetic acid (8.8_5 and 8.9_7 kcal/mol) are larger than for thioacetic acid (7.0 and 7.3 kcal/mol),[26] as expected, and the free energy difference for **1** is smaller (0.05_5 kcal/mol for **1** in 1:3:1 CHF_3, $CHClF_2$, $CHCl_2F$ vs 0.3 kcal/mol for thioacetic acid[26] in $CHClF_2$).[27] The finding of a large amount of the *E* isomer is consistent with the lack of aromaticity[18] of the *Z* conformation, as the acidic hydrogen cannot complete an aromatic sextet. Some of the earlier studies of dithio acids should be re-interpreted, in view of the large amounts of dimer and trimer found under some conditions. We are continuing our NMR studies of dithio acids.

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Novel Organic Ions of High-Spin States: ESR Detection of a Monoanion of *m*-Phenylenebis(phenylmethylene)

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Takeji Takui,[‡] and Koichi Itoh[*,‡]**

Contribution from the Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan, and Department of Chemistry, Faculty of Science, Osaka City University, Osaka 558, Japan. *Received November 10, 1989*

Abstract: 1,3-Bis(α-diazobenzyl)benzene (1,3-BDB), known as the precursor of the spin-quintet *m*-phenylenebis(phenylmethylene) (*m*-PBPM), has been subject to a sequential treatment of γ-radiolysis followed by photolysis in 2-methyltetrahydrofuran at 77 K. ESR and optical measurements indicate the formation of a monoanion of *m*-PBPM. The spin multiplicity in the ground state is doublet but is quartet in the first excited state, the energy gap between the two states being only 4.5 ± 0.5 cm^{-1} as estimated from the temperature dependence of the ESR signal over 3.1–77 K. The present work seems to be the first report of the electronically charged hydrocarbon with high-spin states.

As a model for organic ferromagnets, one of our groups in Osaka has been studying, during the past two decades, aromatic polycarbenes with spin multiplicities up to 11.[1-5] It has now been firmly established that spin alignment in these neutral high-spin molecules is dictated by the topology of the π-electron network.[1d,h,2f-h]

With the intention of developing new aspects of such high-spin molecules, we have attempted to prepare charged high-spin aromatics that may be potentially interesting not only from an experimental but also from a theoretical viewpoint. A brief predictive discussion of charging the neutral high-spin molecules has been made by Yamaguchi.[6] As a prototype of charged polycarbenes a monoanion of *m*-phenylenebis(phenylmethylene) (*m*-PBPM) has been generated for the first time, and the ground and the first excited states have been characterized by ESR.

The method of generation will be described in the subsequent section, but the general feature of the method is briefed here: the group in Kyoto has demonstrated that γ-ray irradiation of dilute frozen solutions of a solute in 2-methyltetrahydrofuran (MTHF) leads to a selective formation of the radical anion of the solute via attachment of electrons that are generated by ionization of the matrix MTHF molecule.[7] This has been verified for several hundred cases by recording the electronic absorption spectrum characteristic of the radical anion of the solute molecules.[8] Thus, it is expected that the irradiation of 1,3-BDB dissolved as the solute in MTHF yields the radical anion of 1,3-BDB. By analogy with

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[†] Kyoto University.

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