

Anisotropic Knight shifts and spin density distribution in β -(BEDT-TTF)₂I₃

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High-resolution ¹³C NMR spectra of the organic metal β -(BEDT-TTF)₂I₃ exhibit lines of all ten crystallographically nonequivalent nuclei. The BEDT-TTF cation-radical spin-density distribution is determined from the Knight shifts and from their anisotropy. The conformational transitions are found to occur exclusively in one-half of the BEDT-TTF molecule.

1. Quasi-two-dimensional metals with bis-(ethylene dithiolo)-tetrathiofulvalene (BEDT-TTF) have currently the highest (for organic compounds) superconducting transition temperatures, reaching 7.5 K for β -(BEDT-TTF)₂I₃ (Refs. 1 and 2). In the present letter we show that the electronic structure of this class of compounds can be studied by means of high-resolution NMR of ¹³C. This method was used previously to study the isotropic Knight shifts^{3–6} and the carbon-atom spin-density distributions⁶ in some other organic compounds. An important difference in β -(BEDT-TTF)₂I₃ is that the Knight shift in it is strongly anisotropic, allowing the spin density in carbon and sulfur atoms in a BEDT-TTF radical to be determined. The spin density of sulfur is of interest because the S–S intermolecular coupling plays, as has been established elsewhere,⁷ the key role in the formation of a two-dimensional conduction band. New data on the conformational transitions in β -(BEDT-TTF)₂I₃ have also been obtained.

2. The experiments were carried out with the Bruker SHR-200 pulse spectrometer in a 47-kG magnetic field at room temperature. A high resolution was achieved by making use of the rapid rotation of the sample (4.3 kG) at the magnetic angle and the decoupling with protons. The spectra (70 000 events, recording time 20 hours) were measured by the method of polarization transfer from protons or by direct excitation by a 90° rf pulse. In the second case, we studied the signal-to-noise ratio of the central BEDT-TTF carbons. The sample contained 21 mg of chemically oxidized,^{2,8,9} ran-

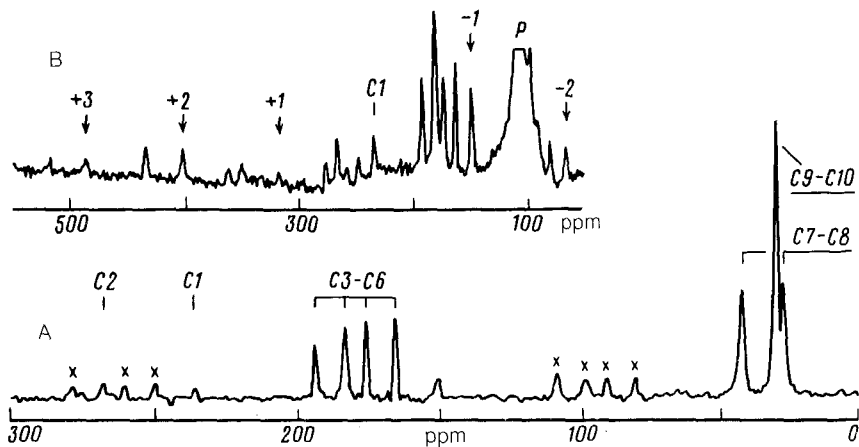


FIG. 1. High-resolution NMR spectra of C for β -(BEDT-TTF) $_2$ I $_3$. A—with polarization transfer (\times —side bands), B—with direct excitation (the arrows indicate the side bands of the C 1 line, P—background signal of the NMR detector).

domly oriented β -(BEDT-TTF) $_2$ I $_3$ crystals. The Knight shifts were reckoned from the position of the corresponding lines in the spectrum of polycrystalline BEDT-TTF.

3. The spectrum and the classification of its lines are shown in Fig. 1. All molecules in β -(BEDT-TTF) $_2$ I $_3$ are crystallographically equivalent,⁷ and Fig. 2A shows 10 nonequivalent carbon positions, C 1–C 10. Distinct lines are resolved for C 1–C 6. Three lines 28.3, 31.2, and 43.3 m.f. with the intensities 1:2:1 correspond to four nuclei C 7–C 10. Of these three lines the strong line has the shortest spin-lattice-relaxation time. To explain this situation, we must take into account the conformational transitions in β -(BEDT-TTF) $_2$ I $_3$, which were detected from the proton relaxation.⁸ The strong line should be assigned to the moving C $_2$ H $_4$ group and the two other lines should be assigned to the stationary C $_2$ H $_4$ group, since the motion suppresses the carbon non-

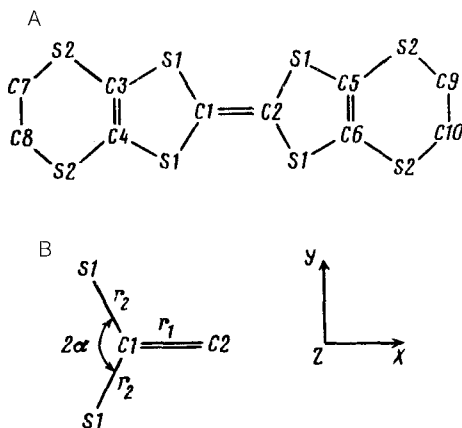


FIG. 2. Structural formula of the BEDT-TTF molecule (A) and its C $_2$ S $_2$ fragment (B).

equivalence and intensifies the relaxation as a result of modulation of the carbon-proton dipole interaction. The conformational transitions thus occur only in half of the molecules, consistent with the structural data on the position-dependent disordering of one of the two C_2H_4 groups.⁷

4. A comparison with the BEDT-TTF spectra shows that, with the exception of $C7-C10$, the β -(BEDT-TTF)₂I₃ lines undergo an isotropic paramagnetic Knight shift: 114 and 146 m.f. for $C1$ and $C2$ (130 m.f., on the average) and 55, 65, 73, and 83 m.f. for $C3-C6$ (69 m.f., on the average). The Knight shift is $K_i = a_i \rho_i X / 2\hbar \gamma_C N_0$ for the nucleus in the position specified by index i , where a_i is the hyperfine coupling constant, ρ_i is the spin density normalized to one for the BEDT-TTF radical, $X = 4.2 \times 10^{-4}$ cm³/mole is the paramagnetic susceptibility,⁹ γ_C is the gyromagnetic ratio of ¹³C, and N_0 is Avogadro's number. The value of a_i is the same for $C1-C6$ in identical C_2S_2 molecular fragments (Fig. 2). Accordingly, $K_i \propto \rho_i$ and the average spin density of $C1$ and $C2$ is twice as high as that of $C3-C6$. This indicates that the quantum chemical calculations which are based on the CNDO/2 method and which yield the same spin density of $C1-C6$ are unreliable.¹⁰

5. As can be seen from Fig. 1B, in addition to the principal $C1$ line, there are several side bands of this line due to the sample rotation, which indicates that the displacement tensor δ_{lm} is strongly anisotropic. Because of the symmetry of the C_2S_2 fragment, the principal axis of the chemical-displacement tensor δ_{lm}^{CS} is the same as that of the Knight-shift tensor K_{lm} and is directed as shown in Fig. 2B. The principal values of δ_{lm} and δ_{lm}^{CS} can be determined from the ratio of the intensities of the side bands to the principal band in the spectra of β -(BEDT-TTF)₂I₃ and BEDT-TTF, respectively, according to the method of Ref. 11. We obtained the following values: $\delta_{ll} = -227, -129, \text{ and } 356$ m.f. and $\delta_{ll}^{CS} = -76.25$ and 51 m.f., but the correspondence of these values with the axes is not known because we used polycrystalline samples. Six different δ_{lm} and δ_{lm}^{CS} each and hence 36 Knight-shift tensors $K_{lm} = \delta_{lm} - \delta_{lm}^{CS}$, which are chosen below on the basis of the criteria for the permissible spin-density values, can be generated through permutation.

Using the $2p_z$ contribution (the contribution of the orbital of the $C1$ atom) and the contributions of the neighboring $C2$ and $S1$ atoms in the point-dipole approximation, we can write

$$\begin{aligned} K_{xx} &= (X/2N_0)[-b\rho_{C1} + 2r_1^{-3}\rho_{C2} + 2(3\cos^2\alpha - 1)r_2^{-3}\rho_{S1}], \\ K_{yy} &= (X/2N_0)[-b\rho_{C1} - r_1^{-3}\rho_{C2} + 2(3\sin^2\alpha - 1)r_2^{-3}\rho_{S1}], \\ K_{zz} &= (X/2N_0)[2b\rho_{C1} - r_1^{-3}\rho_{C2} - 2r_2^{-3}\rho_{S1}]. \end{aligned} \quad (1)$$

Here α , r_1 , and r_2 are the angle and the bond lengths⁷ in Fig. 2B, $b = \pi B_0 / \mu_B \gamma_C$, and $B_0 = 91$ MHz is the anisotropic hyperfine coupling constant of a free carbon atom.¹² Two of the three equations in (1) are linearly independent equations, since $K_{xx} + K_{yy} + K_{zz} = 0$. Substituting $\rho_{C2} = \rho_{C1} K_2 / K_1 = 1.28\rho_{C1}$ in them, we find ρ_{C1} and ρ_{S1} . We then find from ρ_{C1} the value of ρ_i for $C2-C6$ ($\rho_i = 0$ for $C7-C10$, since $K_i = 0$) and the value of ρ_{S2} from the spin-density normalization condition.

The ambiguity of K_{lm} accounts for 36 spin-density distributions, of which only two (the second solution is enclosed in parentheses) $K_{xx} = -154$ (-151), $K_{yy} = -155$ (-180), $K_{zz} = 305$ (331) m.f., $\rho_{C1} = 0.12$ (0.12), $\rho_{S1} = 0.37$ (0.20), $\rho_{S2} = -0.26$ (-0.09) satisfy the conditions for the restriction of the local spin density, $|\rho_i| < 1$, and for its decrease outside the region of polyconjugation of the molecule, $|\rho_{S2}| < |\rho_{S1}|$. Despite the absence of rigorous proof, these conditions are satisfied for the organic radicals and may be viewed as empirical rules governing their behavior.¹² Because of the common features of the two solutions, we can draw the following conclusions. First, the spin-density distributions for carbon are identical and therefore are uniquely determined. Secondly, the opposite signs of ρ_{S1} and ρ_{S2} account for their appreciable absolute values and for the considerable contribution of the intermolecular S - S coupling to the formation of the conduction band. The results of this study can be used for the calculation of the band structure of BEDT-TTF compounds.

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