apparently the relationship between the oscillating and electronic motions, which is the prerequisite for manifestation of the Jahn—Teller effect. Presumably, the occurrence of this relationship accounts for the short spin—lattice relaxation times in C_{60}^- and C_{60}^+ . The width of the C_{120}^+ ESR line at room temperature is of the same order of magnitude as those for radical cations of aromatic hydrocarbons.¹

The results obtained make it possible to conclude that on dissolution of C_{60} crystals in sulfuric acid, in addition to oxidation of molecules, cation dimerization and oligomerization occur at relatively high local concentrations of C_{60} and probably also on the crystal surface. The reaction of a toluene solution of C_{60} ($4 \cdot 10^{-3}$ mol L⁻¹) with a tenfold excess of sulfuric acid proceeds at such reactant ratios at which the rate of cation oligomerization is insignificant.

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Sulfur ylides 8.* Synthesis of 5-methylthio-7,8-dihydro-4,8a-diazafluorene-6,9-dione

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Intramolecular cyclization of ketostabilized sulfur ylide obtained from β -alanine and 2,3-pyridinedicarboxylic anhydride was studied. The structure of the reaction product, 5-methylthio-7,8-dihydro-4,8a-diazafluorene-6,9-dione, was established by X-ray diffraction analysis.

Key words: ketostabilized sulfur ylides, intramolecular cyclization, 5-methylthio-7,8-dihydro-4,8a-diazafluorene-6,9-dione.

In our previous works, i^{-6} we described the synthesis and chemical properties of phthalimido-containing ketostabilized sulfur ylides obtained from α -, β , γ -, and δ -amino acids and phthalic anhydride, as well as the influence of substituents in the phthalimide fragment on the regioselectivity of intramolecular cyclization of sul-

* For Part 7, see Ref. 1.

fur ylides obtained from β -alanine and substituted phthalic anhydrides. The intramolecular cyclization results in the formation of compounds with the structure of indolizidine-2,6-dione.¹⁻⁶

In continuation of the study of the intramolecular cyclization observed, we studied the behavior of ketostabilized sulfur ylide (1) obtained from β -alanine and pyridine-2,3-dicarboxylic anhydride. Ylide 1 containing pyridine-2,3-dicarbimide fragment was obtained

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in a satisfactory yield (52%) from hydrobromide of sulfonium salt (2), which was synthesized from protected β -alanine (3) according to the scheme developed⁴ by us. Two isomers can be formed during the intramolecular cyclization of 1. However, taking into account the nucleophilic character of sulfur ylide, we can assume that the interaction of the carbanion with the more electron-deficient carbinide carbon atom in the β -position to the nitrogen atom of the pyridine ring and, as a consequence, the formation of tricyclic compound (4), are preferable.

Heating of sulfur ylide 1 in a toluene solution in the presence of an equimolar quantity of benzoic $acid^2$ resulted in the formation of the single compound. Since the data of ¹H and ¹³C NMR spectroscopy gave no unambiguous proof of the structure, we carried out the X-ray diffraction analysis and established unambiguously the structure of compound 4. The general view of molecule 4 is shown in Fig. 1, and the coordinates of atoms are presented in Table 1.



Experimental

IR spectra were obtained on a Specord M-80 instrument. ¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 spectrometer with a working frequency of 300 and 75 MHz, respectively, using TMS as the internal standard.

Crystals 4, $C_{12}H_{10}N_2O_2S$, are triclinic; at 23 °C, a = 7.615(4), b = 8.095(7), c = 10.256(2) Å, $\alpha = 79.20(5)$, $\beta = 75.94(3)$, $\gamma = 63.88(3)^\circ$, V = 548.25 Å³, z = 2, $d_{calc} = 1.492$ g cm⁻³, space group PI.

Cell parameters and intensities of 1178 reflections with $F^2 \leq 36$ were measured on an Enraf-Nonius CAD-4 automated diffractometer (λ MoK α radiation, graphite monochromator, $\omega/20$ -scan, $20 \leq 60^{\circ}$).



Fig. 1. General view of molecule 4.

Table 1. Coordinates of atoms in structure 4

Atom	x	у	z
S	0.7715(1)	0.37731(8)	0.39059(6)
O(2)	1.1185(3)	0.1582(2)	0.5208(2)
O(6)	1.3949(2)	-0.1181(2)	-0.0524(2)
N(5)	1.2248(2)	0.0165(2)	0.1459(2)
N(10)	0.8101(3)	0.4252(2)	0.0547(2)
C(1)	1.0011(3)	0.2107(3)	0.3191(2)
C(2)	1.1516(3)	0.1204(3)	0.4061(2)
C(3)	1.3564(3)	-0.0104(4)	0.3412(2)
C(4)	1.3429(3)	-0.1151(3)	0.2401(2)
C(6)	1.2560(3)	0.0061(3)	0.0082(2)
C(6a)	1.0953(2)	0.1665(2)	-0.0424(2)
C(7)	1.0558(3)	0.2316(3)	-0.1711(2)
C(8)	0.8922(3)	0.3941(3)	-0.1847(2)
C(9)	0.7744(3)	0.4857(3)	-0.0715(3)
C(10a)	0.9674(3)	0.2668(2)	0.0663(2)
C(10b)	1.0520(3)	0.1719(2)	0.1880(2)
C(11)	0.5940(4)	0.3337(4)	0.3323(3)

The structure was solved using the MULTAN program and refined in the anisotropic approximation.⁷ Hydrogen atoms were revealed from the differential synthesis and refined in the isotropic approximation. The resulting values of divergence factors are $R = R_w = 0.031$.

All calculations were performed on a PDP-11/23 computer by the SDP program.

3-(Pyridine-2,3-dicarbimido)propionic acid (3). A mixture of β -alanine (5.3 g, 0.06 mol) and thoroughly powdered pyridine-2,3-dicarboxylic anhydride (8.9 g, 0.06 mol) was heated at 145–150 °C for 30 min. After cooling, the solid reaction product was dissolved in hot MeOH (40 mL), the solution was filtered and diluted with 40 mL of water, and the residue that formed was filtered off and dried. Compound 3 with m.p. 160–161 °C (EtOH) was obtained in 50% yield (6.6 g). Found (%): C, 54.68; H, 3.45; N, 12.81. C₁₀H₈N₂O₄. Compound (%): C, 54.55; H, 3.66; N, 12.72. IR, v/cm⁻¹: 1600, 1690, 1725, 1785. ¹H NMR (acetone-d₆), 8: 2.73 (t, 2 H, CH₂, J = 7.0 Hz); 3.98 (t, 2 H, CH₂, J = 7.0 Hz); 7.06–9.17 (m, 3 H, C₅H₃N).

1-Bromo-4-(pyridine-2,3-dicarbimido)butan-2-one hydrobromide (5). SOCl₂ (3.6 g, 0.03 mol) was added to a suspension of compound 3 (2.2 g, 0.01 mol) in anhydrous benzene (50 mL). The mixture was boiled with a reflux condenser for 2 h. The solvent and an excess of SOCl₂ were distilled off. Then an ethereal solution of diazomethane obtained from nitrosomethylurea (4.1 g, 0.04 mol) was placed in a threenecked flask with a stirrer, a dropping funnel, and a thermometer. A solution of acid 3 chloride obtained in ether (10 mL) was added dropwise with stirring at 0 °C, and after the end of nitrogen evolution, the reaction mixture was additionally stirred for 1 h. Then concentrated HBr (10 mL) was added with stirring to the suspension of diazoketone obtained. After HBr was added, the reaction mixture was boiled with a reflux condenser for 1 h and cooled. The ether was distilled off, and the residue was washed with an aqueous solution of NaHCO3 and water. After drying in a desiccator, bromoketone hydrobromide 5 with p.decomp. >230 °C was obtained (3.4 g, 90%). Found (%): C, 34.70; H, 2.65; Br, 42.40; N, 7.38. C₁₁H₉BrN₂O₃ · HBr. Calculated (%): C, 34.95; H, 2.67; Br, 42.27; N, 7.41. IR. v/cm⁻¹: 1640, 1736, 1792, 2040, 2096, 2320. ¹H NMR (DMSO-d₆), δ : 3.10 (t, 2 H, CH₂, J = 7.0 Hz); 3.70 (t, 2 H, CH_2 , J = 7.0 Hz); 4.00 (s, 2 H, CH₂Br); 7.80–9.00 (m, 3 H, C₅H₃N). ¹³C NMR (DMSO-d₆), δ: 32.8 (C-1); 36.9 (C-3); 37.5 (C-4); 127.3 (C-12); 127.9 (C-10); 131.3 (C-11); 151.5 (C-7); 154.8 (C-9); 166.0 (C-13); 166.1 (C-6); 199.7 (C-2).

Hydrobromide of 4-(pyridine-2,3-dicarbimido)-2-oxobut-1-yldimethylsulfonium bromide (2). Me₂S (0.9 g, 0.015 mol) was added with stirring to bromoketone 2 (1.9 g, 0.005 mol) in acetone (50 mL), and the reaction mixture was let to stand at -20 °C for 10--14 h. The residue was filtered off, washed with acetone, and dried in a desiccator. Compound 2 (2.3 g, 81%) with m.p. 113--115 °C was obtained. Found (%): C, 35.38; H, 3.51; Br, 36.15; N, 6.22; S, 7.34. C₁₃H₁₅BrN₂O₃S ·HBr. Calculated (%): C, 35.47; H, 3.66; Br, 36.30; N, 6.36; S, 7.28. IR, v/cm⁻¹: 1712, 1736, 1792. 2032, 2292. ¹H NMR (CF₃COOH), &: 2.67 (s, 6 H, SMe₂); 3.0 (t, 2 H, CH₂, J = 7.0 Hz); 3.86 (t, 2 H, CH₂, J =7.0 Hz); 4.56 (s, 2 H, CH₂S); 7.80-9.10 (m, 3 H, C₅H₃N).

1-Dimethylsulfonium-4-(pyridine-2,3-dicarbimido)-2-oxobutan-1-ide (1). A 12.5 M solution (0.7 mL) of NaOH and a saturated solution of K_2CO_3 (4 mL) were added to a suspension (cooled to 10 °C) of sulfonium sait 2 (2.2 g, 0.005 mol) in CHCl₃ (10 mL). The reaction mixture was stirred for 15 min, the temperature was brough to ~20 °C, the residue of inorganic salt was filtered off, and the organic layer was dried over K_2CO_3 . After the solvent was distilled off, compound 1 (0.72 g, 52%) was obtained as a yellow viscous oil. Found (%): C, 55.98; H, 5.01; N, 10.22; S, 11.34. $C_{13}H_{14}N_2O_3S$. Calculated (%): C, 56.10; H, 5.07; N, 10.06; S, 11.52. IR, v/cm⁻¹: 1548, 1722, 1782. ¹H NMR (CDCl₃), δ : 2.57 (t, 2 H, CH₂, J = 7.0 Hz); 4.05 (t, 2 H, CH₂, J = 7.0 Hz); 3.65 (s, 1 H, CHS); 7.80-9.00 (m, 3 H, C₅H₃N). ¹³C NMR (CDCl₃), δ : 28.2 (Me₂S); 36.9 (C-4); 43.8 (C-3); 52.2 (C-1); 124.9 (C-12); 125.9 (C-10); 131.7 (C-11); 150.5 (C-7); 153.4 (C-9); 166.0 (C-13); 169.2 (C-6); 185.7 (C-2).

5-Methylthio-7,8-dihydro-4,8a-diazafluorene-6,9-dione (4). A mixture of sulfur ylide 1 (0.6 g, 0.002 mol) and benzoic acid (0.2 g, 0.002 mol) was dissolved upon heating in anhydrous toluene (8 mL). The mixture was boiled with a reflux condenser for 1.5 h. Toluene was evaporated, and the residue was chromatographed on SiO₂ (AcOEt : hexane, 1 : 1) to isolate compound 4 (0.3 g, 58%) with m.p. 184--185 °C. Found (%): C, 58.25; H, 4.12; N, 11.34; S, 12.96. C₁₂H₁₀N₂O₂S. Calculated (%): C, 58.52; H, 4.09; N, 11.37; S, 13.02. ¹H NMR (CDCl₃), & 2.54 (s, 3 H, CH₃S); 2.90 (t, 2 H, CH₂, J = 7.3 Hz); 4.20 (t, 2 H, CH₂, J = 7.3 Hz); 7.60--9.08 (m, 3 H, C₅H₃N). ¹³C NMR (CDCl₃), & 18.2 (CH₃S); 36.3 (C-3); 36.8 (C-4); 116.9 (C-1); 124.4 (C-6a); 124.9 (C-7); 131.6 (C-8); 146.1 (C-10a); 153.9 (C-9); 154.5 (C-10b); 162.9 (C-6); 190.7 (C-2).

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