analogous constant for $C_{60}P(O)(OPr^i)_{2}$,⁵ since one of the double bonds nearest to the radical center is excluded from conjugation because of the addition of the metallocomplex (cf. Ref. 2). It is known that the density of the unpaired electron in the fullerenyl radicals is mainly delocalized over two six-membered cycles adjacent to the C-CR bond.^{6,7} Demetalation of the metallocomplex occurs when the sample is heated to 370 K and the ESR spectrum of $C_{60}P(O)(OPr^i)_2$ radical is recorded (Fig. 1, d).

An analogous picture is observed for the radical adducts of the phosphoryl radicals with metallocomplex 2. A broad signal ($a_P = 62.7$ G, g = 2.0028) dominates immediately after photolysis was begun.

Thus, it is likely that a characteristic feature of the radical adducts of metallocomplexes of C_{60} with Ir is the addition of the phosphoryl radicals at a distance of two—three bond lengths from the metal atom. This might be caused by a stronger distortion of the polyhedron in the iridium metallocomplex than that in the complexes of fullerene with Pt and Pd because of stronger binding of Ir with fullerene.

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References

- B. L. Tumanskii, V. V. Bashilov, N. N. Bubnov, S. P. Solodovnikov, and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 938 [*Russ. Chem. Bull.*, 1994, 43, 884 (Engl. Transl.)].
- B. L. Tumanskii, M. N. Nefedova, V. V. Bashilov, N. N. Bubnov, S. P. Solodovnikov, and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 3015 [*Russ. Chem. Bull.*, 1996, 45, 2865 (Engl. Transl.)].
- A. V. Usatov, K. N. Kudin, E. V. Vorontsov, L. E. Vinogradova, and Yu. N. Novikov, J. Organomet. Chem., 1996, 522, 147.
- 4. A. V. Usatov, E. V. Vorontsov, L. E. Vinogradova, and Yu. N. Novikov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1661 [*Russ. Chem. Bull.*, 1994, **43**, 1572 (Engl. Transl.)].
- B. L. Tumanskii, V. V. Bashilov, S. P. Solodovnikov, and V. I. Sokolov, *Izv. Akad. Nauk. Ser. Khim.*, 1992, 1457 [*Bull. Russ. Acad. Sci.*, *Div. Chem. Sci.*, 1992, **41**, 1140 (Engl. Transl.)].
- 6. J. R. Morton, K. F. Preston, P. J. Krusic, S. A. Hill, and E. Wasserman, J. Phys. Chem., 1992, 9, 3576.
- B. L. Tumanskii, V. V. Bashilov, E. N. Shaposhnikova, N. N. Bubnov, S. P. Solodovnikov, and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2679 [Russ. Chem. Bull, 1996, 45, 2530 (Engl. Transl.)].

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Reaction of hydroxyiminoacetophenone with *p*-toluenesulfonyl chloride and an X-ray diffraction study of the reaction product

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2-Benzoyloxy-2-phenylmalononitrile is formed instead of the expected oxime tosylate in the reaction of hydroxyiminoacetophenone with p-toluenesulfonyl chloride. The structure of the product was confirmed unambiguously by X-ray diffraction analysis.

Key words: hydroxyiminoacetophenone; *p*-toluenesulfonyl chloride; 2-benzoyloxy-2-phenylmatononitrile; X-ray diffraction analysis.

Previously,¹ the *p*-toluenesulfonate of oxomalononitrile oxime used for the synthesis of substituted cyanopyrazines² has been prepared by tosylation of hydroxyiminomalononitrile. We attempted to synthesize the *p*-toluenesulfonate of phenylglyoxal oxime in order to use it for similar purposes. However, the ¹H NMR

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Fig. 1. General view of molecule 6.

spectrum of the product prepared by treatment of the initial hydroxyimino derivative 1 with TsCl in dry pyridine (Scheme 1) exhibited no signals typical of the tosyl group but contained only signals of aromatic protons. The ¹³C NMR spectrum did not permit unambiguous determination of the structure of the product, and mass and IR spectra provided little information; therefore,

Table 1. Bond lengths (d) in molecule 6

Bond	d/Å	Bond	d/Å
$\overline{O(1) - C(7)}$	1.436(3)	C(5) - C(6)	1.386(4)
O(1) - C(10)	1,381(3)	C(7) - C(8)	1.484(3)
O(2) - C(10)	1.199(3)	C(7) - C(9)	1.486(3)
N(1) - C(9)	1.138(3)	C(10) - C(11)	1.474(3)
N(2) - C(8)	1.136(3)	C(11) - C(12)	1.383(3)
C(1) - C(2)	1.383(3)	C(11) - C(16)	1.390(3)
C(1) - C(6)	1.382(4)	C(12) - C(13)	1.381(4)
C(1) - C(7)	1.532(3)	C(13)-C(14)	1.378(4)
C(2) - C(3)	1.391(4)	C(14) - C(15)	1.378(4)
C(3) - C(4)	1.375(4)	C(15) - C(16)	1.379(4)
C(4)-C(5)	1.382(4)		

Table 2. Bond angles (ω) in molecule 6

Angle	ω/deg	Angle	ω/deg
$\overline{C(7)-O(1)-C(10)}$	115.3(2)	C(8) - C(7) - C(9)	108.7(2)
C(2) - C(1) - C(6)	121.1(2)	N(2) - C(8) - C(7)	177.5(3)
C(2) - C(1) - C(7)	120.2(2)	N(1) - C(9) - C(7)	175.1(2)
C(6) - C(1) - C(7)	118.5(2)	O(1) - C(10) - O(2)	121.3(2)
C(1) - C(2) - C(3)	118.8(2)	O(1) - C(10) - C(11)	112.5(2)
C(2) - C(3) - C(4)	120.3(2)	O(2) - C(10) - C(11)	126.2(2)
C(3) - C(4) - C(5)	120.4(2)	C(10) - C(11) - (12)	122.9(2)
C(4) - C(5) - C(6)	119.8(3)	C(10) - C(11) - (16)	116.7(2)
C(1) - C(5) - C(5)	119.4(2)	C(12) - C(11) - (16)	120.5(2)
O(1) - C(7) - C(1)	108.2(2)	C(11) - C(12) - (13)	119.3(2)
O(1) - C(7) - C(8)	108.2(2)	C(12) - C(13) - (14)	120.3(3)
C(1) - C(7) - C(8)	112.1(2)	C(13) - C(14) - (15)	120.3(3)
O(1) - C(7) - C(9)	H1.5(2)	C(14) - C(15) - (16)	120.0(2)
C(1) - C(7) - C(9)	108.2(2)	C(11) - C(16) - (15)	119.6(3)



this compound was studied by X-ray diffraction analysis. Figure 1 shows the general view of molecule 6. The bond lengths, bond angles, and coordinates of atoms are listed in Tables 1, 2, and 3 (heat parameters are available from the authors).

According to the Cambridge Crystallographic Database,³ no data on the structures of compounds of this type have been reported.

Three planar fragments can be distinguished in the molecule: C(1)...C(6) (A), C(11)...C(16) (B), and C(1)-C(7)-O(1)-C(10)-C(11) (plane C is accurate to within ± 0.038 Å). The magnitudes of dihedral angles, A/B 50.6°, A/C 42.3°, and B/C 10.1°, indicate that the molecule is markedly twisted with respect to the central fragment; apparently, this is due to the presence of forced intramolecular steric nonvalence contacts: O(1)...C(6) 2.785 (3), O(1)...C(12) 2.758(3), O(2)...C(8) 2.784(3), O(2)...C(9) 2.649(3), O(2)...C(16) 2.823(3), C(2)...C(8) 2.851(3), C(2)...C(9) 3.302(3) Å (the sum of the van der Waals radii of O and C is 3.22 Å, and twice the van der Waals radius of C is 3.40 Å⁴). The substantial deviations of the C(9)C(8)N(2) (177.5(3)°) and C(7)C(9)N(1) (175.1(2)°) bond angles from 180° and of the O(1)C(10)C(11) (112.5(5)°), O(2)C(10)C(11)(126.2(2)°), and C(10)C(11)C(16) (116.7(2)°) bond angles from 120° can be explained by the contacts mentioned

Table 3. Atomic coordinates in molecule 6 (×10⁴; for H, ×10³)

Atom	x	у	ζ	-
0(1)	1172(3)	8719(1)	1242(1)	-
O(2)	-1417(3)	7678(1)	1175(1)	
N(I)	-2094(4)	8593(2)	2225(1)	
N(2)	-3145(4)	9753(2)	830(1)	
C(1)	898(4)	10164(1)	1650(1)	
C(2)	-41(4)	11017(2)	1644(1)	
C(3)	1019(5)	11754(2)	1847(1)	
C(4)	2965(5)	11632(2)	2051(1)	
C(5)	3903(5)	10778(2)	2050(1)	
C(6)	2860(4)	10037(2)	1851(1)	
C(7)	-301(4)	9322(2)	1470(1)	
C(8)	-1942(4)	9567(2)	1115(1)	
C(9)	-1325(4)	8876(2)	1888(1)	
C(10)	351(4)	7897(2)	1083(1)	
C(11)	1870(4)	7366(2)	797(1)	
C(12)	3809(4)	7707(2)	663(1)	
C(13)	5124(4)	7172(2)	386(1)	
C(14)	4518(5)	6306(2)	249(1)	
C(15)	2590(5)	5965(2)	384(1)	
C(16)	1254(5)	6492(2)	658(1)	
H(2)	-138(5)	1109(2)	148(1)	
H(3)	34(5)	1236(2)	190(1)	
H(4)	368(4)	1213(2)	220(1)	
H(5)	527(4)	1067(2)	220(1)	
H(6)	345(4)	945(2)	185(1)	
H(12)	422(4)	826(2)	76(1)	
H(13)	650 <u>(</u> 4)	743(2)	30(1)	
H(14)	546(5)	594(2)	5(1)	
H(15)	219(5)	537(2)	28(1)	
H(16)	-16(4)	628(2)	76(1)	

above. The rest of the bond lengths and angles have normal⁵ magnitudes.

These compounds are dimers of the nitriles of substituted glyoxylic acids (in this particular case, phenylglyoxylic acid) and are prepared by the reaction of the corresponding acid halide either with Hg(CN)₂,⁶ AgCN,⁷ or CuCN⁸ or with sodium cyanide under the conditions of phase transfer catalysis.⁹ Based on the structure of the compound synthesized and the published data, the following scheme of transformations can be suggested.

The tosylate 2 formed initially eliminates a proton under the action of pyridine, and then eliminates TsO⁻. The resulting nitrile 3 reacts with pyridine to give salt 4, which dissociates thus generating CN⁻. The cyanide ion adds to the carbonyl carbon atom of another benzoyl cyanide molecule to give intermediate 5; the latter is benzoylated by salt 4. Finally, compound 6 is formed.

Experimental

¹H NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz), and IR spectra were obtained on a UR-20 instrument. Mass spectra were measured on a Varian MAT 311A mass spectrometer. Hydroxyiminoacetophenone 1 was synthesized by a known procedure.¹⁰

2-Benzoyloxy-2-phenylmalononitrile (6): p-Toluenesulfonyl chloride (0.85 g) was added with stirring to a solution of hydroxyiminoacetophenone (0.75 g, 0.005 mol) in 5 mL of dry pyridine. The reaction mixture was kept for 12 h at 18 °C and poured into ice water. The precipitate was filtered off and recrystallized from a chloroform-pentane mixture to give 0.2 g of the product, m.p. 96-98 °C (cf. Refs. 6 and 7, m.p. 96-98 °C). Crystals of compound 6 are orthorhombic; at -80 °C, a = 6.369(2), b = 14.603(4), c = 27.888(6) Å, V = 2594(2) Å³, $d_{calc} = 1.343$ g cm⁻³, space group Pbca, Z = 8. Unit cell parameters and intensities of 2683 independent reflections were measured on a Syntex P21 four-circle automatic diffractometer (λ Mo-K α -radiation, graphite monochromator, $\theta/2\theta$ -scanning up to $\theta_{max} = 25^{\circ}$). The structure was solved by the direct method, which revealed all the nonhydrogen atoms, and refined by the full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms over 1484 reflections with $I > 3\sigma(I)$. All the hydrogen atoms were objectively revealed by differential synthesis and refined isotropically. The final residual values were R = 0.038 ($R_w =$ 0.038). All the calculations were carried out using the SHELXTL PLUS program¹¹ (the PC version).

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References

- 1. J. M. Biechler, J. Perchais and J. P. Fleury, Bull. Soc. Chim. Fr., 1971, 2711.
- 2. J. Perchais and J. P. Fleury, Tetrahedron, 1974, 30, 999.
- 3. Cambridge Crystallographic Database, Cambridge, Release 1996.
- 4. A. Bondi, J. Phys. Chem., 1966, 70, 3006.
- F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, J. Chem. Soc., Perkin Trans. 2, 1987, S1.
- 6. F. Wöhler and J. Liebig, Annalen, 1832, 3, 249.
- 7. H. Habner, Annalen, 1861, 120, 330.
- 8. T. S. Oakwood and C. A. Weisgerber, Org. Synth. Coll., 1955, 3, 112.
- 9. K. E. Koenig and W. P. Weber, Tetrahedron Lett., 1974, 26, 2275.
- 10. P. Zbiorowa, in Preparatyka orgaiczna, Warszawa. 1954, 239.
- W. Robinson and G.M. Sheldrick, in Crystallographic Computing — Techniques and New Technologies, Oxford Univ. Press, Oxford, 1988, 366.