Synthesis of a C_{60} complex with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine and its crystal structure

V. A. Nadtochenko, V. V. Gritsenko, O. A. D'yachenko, G. V. Shilov, and A. P. Moravskii*

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588

The complex of fullerene C_{60} with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) was synthesized and studied by X-ray analysis.

Key words: fullerene C_{60}, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, complex; X-ray analysis.

Fullerene C_{60} is a good electron acceptor[1] and its ground and excited states readily enter redox reactions.[2] It has been shown previously that organic amines possessing electron-donating properties form charge-transfer complexes between C_{60} and amine,[3] which are of interest as promising nonlinear optical materials.[4] It has been reported on the ferromagnetic properties of the C_{60} complex with tetrakis(dimethylamino)ethylene ($C_{60}\cdot$TDAE), one of the representatives of tertiary amines.[5] The complexes of tetrakis(dimethylamino)ethylene have been considered recently as a new state of spin glasses.[6]

Literature data on the crystal structure of C_{60} complexes with tertiary amines are almost nonexistent. The structures of crystallosolvates of C_{60} with benzene ($C_{60}\cdot 4C_6H_6$)[7,8] and CH_2I_2 ($C_{60}\cdot C_6H_6\cdot CH_2I_2$)[9]; intercalates of C_{60} with ferrocene ($C_{60}\cdot[(\eta_5\text{-}C_5H_5)_2Fe]_2$),[10] 1,4-hydroquinone ($C_{60}\cdot(HQ)_3$),[11] bis(ethylenethio)-tetrathiafulvalene ($C_{60}\cdot$(BEDT-TTF)$_2$),[12] and sulfur ($C_{60}\cdot 2S_8$);[13,14] solvated intercalates of C_{60} with iodine and toluene ($C_{60}\cdot I_2\cdot$PhMe);[15] and bis(dimethylthieno)tetratellurafulvalene and carbon disulfide ((BDMT-TTeF)$\times$$\times C_{60}\cdot CS_2$),[16] octamethylenetetrathiafulvalene and benzene ((OMTTF)$\cdot C_{60}\cdot C_6H_6$),[17] and "twinned" BEDT-TTF with carbon disulfide (twin(BEDT-TTF)$\times$$\times C_{60}\cdot CS_2$)[18] were reported.

This work describes the synthesis and crystal structure of the C_{60} complex with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD). The composition of the complex $C_{60}\cdot$TMPD was established by the X-ray analysis. Crystals of the complex were grown from a solution of C_{60} and TMPD in chlorobenzene at the concentration ratio [C_{60}] : [TMPD] = 0.001 : 1 (mol L^{-1}). Under these conditions, about 50 % of C_{60} molecules in the solution are bound in the complex.[19] Crystals of $C_{60}\cdot$TMPD are black, their size is suitable for X-ray analysis, and they are formed over a week upon slow evaporation of the solvent followed by washing from the residue of TMPD with acetone. For control experiments, crystals of C_{60} were also obtained from a cholorobenzene solution in the absence of the amine.

The IR spectra of $C_{60}\cdot$TMPD single crystals contain the corresponding absorption bands of C_{60} and TMPD. A weak absorption of chlorobenzene is also observed, which is an order of magnitude weaker than that of C_{60} crystals obtained from the solution in the absence of the amine (the absorption of PhCl is compared relative to that of C_{60}). In addition, the IR spectra of $C_{60}\cdot$TMPD exhibit a red shift of several vibrational bands of C_{60}, especially pronounced for the frequency of 1428 cm^{-1}, and the distortion of some background modes of the vibrational bands of TMPD. These results likely testify to the formation of the $C_{60}\cdot$TMPD complex with the partial charge transfer from the amine molecule to C_{60}. The detailed analysis of the IR spectra of the crystals obtained will be published elsewhere.[20]

According to the data of the X-ray study, [C_{60}] : [TMPD] = 1 : 1. The main crystallographic parameters are: $C_{70}H_{16}N_2$, M = 884.91, triclinic unit cell, a = 10.124(2) Å, b = 10.244(2) Å, c = 10.544(1) Å, α = 78.24(1)°, β = 84.07(1)°, γ = 59.60(2)°, V = 884.8(2) Å^3, space group $P\bar{1}$, Z = 1, d_{calc} = 1.66 g cm^{-3}, F(000) = 450.

The structure was solved by the direct method and refined by the least-squares method in the anisotropic approximation for nonhydrogen atoms to R = 0.15. The calculations were performed by SHELXS-86 and SHELXL-93 program complexes on a PC AT-486. The relatively high value of the R factor is likely explained by some positional disordering of C_{60} molecules in the crystal. The assumption of disordering of C_{60} molecules is confirmed by the observation of a considerable number of peaks of the electron density near the main sites of the carbon atoms of C_{60} in the differential synthesis. The inclusion of these peaks into the calculation and

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1285—1287, May, 1996.

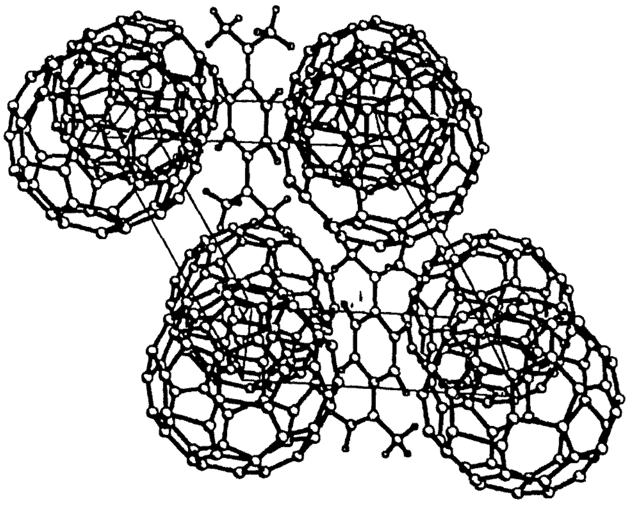

Fig. 1. Crystal structure of $C_{60} \cdot$ TMPD complex.

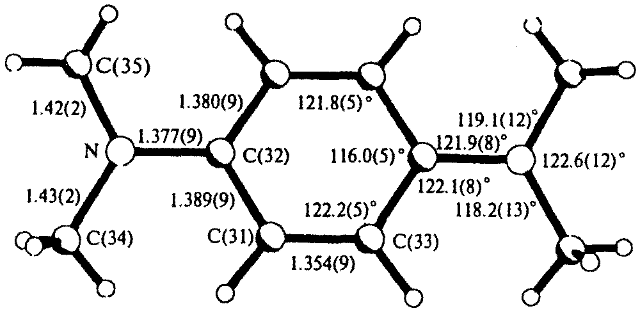

Fig. 2. Molecular structure of TMPD in $C_{60} \cdot$ TMPD complex (bond lengths (Å) and bond angles are indicated).

simultaneous refinement of populations of the main and additional sites of C_{60} atoms result in a decrease in R to 0.08.

The crystal structure of $C_{60} \cdot$ TMPD is layers of TMPD and C_{60} alternating along the b axis (Fig. 1). Molecules of C_{60} are arranged in symmetry centers (0, 0, 0) at the vertices of the cell, and TMPD molecules are localized in symmetry centers (0, 1/2, 1/2) on planes (0yz). The main bond lengths and bond angles in TMPD molecules are presented in Fig. 2. The shortened intermolecular contacts C...C [3.21(2)—3.32(1) Å] (the sum of van der Waals radii of these atoms is equal to 3.42 Å) are determined between C_{60} and TMPD.[21]

This work was performed in the framework of the State Scientific Technical Program "Current Directions in Condensed Matter Physics," direction "Fullerenes and Atomic Clusters" and with the financial support of the Russian Foundation for Basic Research (Projects No. 93-03-5254).

References

1. R. Taylor and D. M. R. Walton, *Nature*, 1993, **363**, 685.
2. A. Hirsch, *Angew. Chem.*, 1993, **105**, 1189; *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 1138.
3. A. I. Kotov, S. V. Konovalikhin, P. V. Pisarev, G. V. Shilov, O. A. Dyachenko, and E. B. Yagubskii, *Mendeleev Commun.*, 1994, 180.
4. Y. Wang, *J. Phys. Chem.*, 1992, **96**, 764.
5. P. M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner, and J. D. Thompson, *Science*, 1991, **253**, 301.
6. K. Prassiedes, in *Fullerenes, Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, Eds. K. Kadish and R. S. Ruoff, The Electrochem. Soc. Inc., Pennington (N. Y.), 1994, 477.
7. M. F. Meidine, P. B. Hitchcock, H. W. Kroto, R. Taylor, and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 1534.
8. A. L. Balch, J. W. Lee, B. C. Noll, and M. M. Olmstead, *J. Chem. Soc., Chem. Commun.*, 1993, 56.
9. U. Geiser, S. K. Kumar, B. M. Savall, S. S. Harried, K. D. Carlson, P. R. Mobley, H. H. Wang, J. M. Williams, and R. E. Botto, *Chem. Mater.*, 1992, **4**, 1077.
10. J. D. Crane, P. B. Hitchcock, H. W. Kroto, R. Taylor, and D. M. R. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 1764.
11. O. Ermer, *Helv. Chim. Acta*, 1991, **74**, 1339.
12. A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito, and H. Shinohara, *J. Chem. Soc., Chem. Commun.*, 1992, 1472.
13. G. Roth and P. Adelmann, *Appl. Phys.*, 1993, **A56**, 169.
14. L. I. Buravov, O. A. D'yachenko, S. V. Konovalikhin, N. D. Kushch, I. P. Lavrent'ev, N. G. Spitsina, G. V. Shilov, and E. B. Yagubskii, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 262 [*Russ. Chem. Bull.*, 1994, **43**, 240 (Engl. Transl.)].
15. P. R. Birkett, C. Christides, P. B. Hitchcock, H. W. Kroto, K. Prassides, R. Taylor, and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1407.
16. P. Wang, W.-J. Lee, I. Shcherbakova, M. P. Cava, and R. M. Metzger, *Synth. Met.*, 1994, **64**, 319.
17. G. Saito, T. Teramoto, A. Otsuka, Y. Sugita, T. Ban, M. Kusunoki, and K. Sakaguchi, *Synth. Met.*, 1994, **64**, 359.
18. A. Izuoka, T. Tachikawa, T. Sugawara, Y. Saito, and H. Shinohara, *Chem. Lett.*, 1992, 1049.
19. V. A. Nadtochenko, N. N. Denisov, I. V. Rubtsov, and P. P. Levin, in *Fullerenes, Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, Eds. K. Kadish and R. S. Ruoff, The Electrochem. Soc. Inc., Pennington (N. Y.), 1994, 1645.
20. A. V. Bazhenov, M. Yu. Maksimuk, T. N. Fursova, A. P. Moravsky, and V. A. Nadtochenko, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1459 [*Russ. Chem. Bull.*, 1996, **45**, No. 6 (Engl. Transl.)].
21. Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.*, 1995, **64**, 446 [*Russ. Chem. Rev.*, 1995, **64** (Engl. Transl.)].

Received August 9, 1995;
in revised form January 15, 1996