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Intramolecular Charge Transfer Interaction in 1,3-Diphenyl-2-pyrazoline Ring-Fused C_{60}

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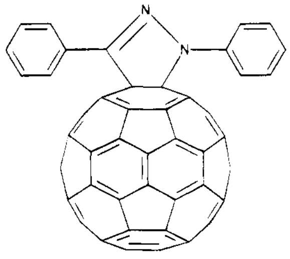
Charge-transfer (CT) interaction between a benzene ring (6π system) and a C_{60} sphere (60 or 58π system with large bond angle strain) is an intriguing research subject. Indeed, already an intermolecular CT interaction between an electropositively substituted benzene and C_{60} has been reported.[1,2] Structurally interesting C_{60} derivatives having benzene ring(s) have also been synthesized;[3] however, to our knowledge the signature of an intramolecular CT interaction between phenyl group(s) and the C_{60} sphere in these C_{60} derivatives has not been observed.

We have been interested in 1,3-diphenyl-2-pyrazoline ring-fused C_{60} (**1**) based on the CPK model, because **1** should be a nice model to examine the competitive intramolecular CT interaction of both phenyl groups with the C_{60} sphere (58π system).



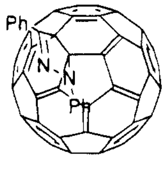
1

As a strategy for the synthesis of **1**[4,5] we have adopted the 1,3-dipolar cycloaddition of 1,3-diphenyl nitrilimine whose dipole is in the reverse direction to that of diazoalkanes.

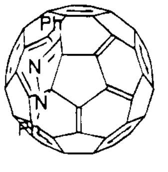
Since the 1,3-dipolar cycloaddition of diazoalkanes to C_{60} does not provide a stable 1,3-dipolar adduct but rather gives decomposition products (methanofullerene and methanofulleroid),[6] this reaction is not appropriate for our purpose.

We report here a typical example of the reaction of C_{60} with 1,3-diphenyl nitrilimine generated in situ, giving a new type of dinitrogen heterocycle-fused C_{60} (1:1 adduct), and characterize this product. In the presence of triethylamine (0.02 mmol) a solution of C_{60} (0.01mmol) and *N*-(α-chrolobenzylidene)-*N*′- phenylhydrazine (0.011mmol) in benzene (10 mL) was refluxed for 2 h. The column chromatographic separation (hexane–benzene/silica gel) of the reaction mixtures provided a stable dark brown product **1** (conversion:61.3%), unreacted C_{60} (22.2%) and di- and triadducts (8.3%) indicating that the reaction proceeded selectively to give **1** (brown powder), mp > 300 °C.

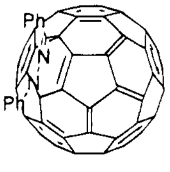
The structure of the major product (**1**) was determined by spectroscopic (MS, IR, NMR, UV–vis) and AM 1 (and also PM 3) analyses.[7] FABMS spectra exhibit the parent ion peak (*m/z*) at 914, and the exact FABMS spectra completely agree with the theoretically predicted pattern of isotopic distribution (found *m/z* 914.0834; calcd for C_{60}-($C_{13}H_{10}N_2$) *m/z* 914.0840). The FT-IR spectra contain both characteristic bands for C_{60} and 1,3-diphenyl-2-pyrazoline (**2**) (see supporting information). Although X-ray diffraction of **1** has not yet been accomplished because of difficulty in growing single crystals for this purpose, the AM1 study clearly indicates that (1) **3a** is the most stable of the three cycloadducts (**3a–c**), (2) **3b** and **3c** are more unstable by 17.5 and 59.0 kcal/mol than **3a**, respectively, and (3) an increase in the bond distance between both sp³ carbon atoms of **3a** (conversion of the bridged fullerene to the corresponding fulleroid) results in the destabilization. The PM 3 investigation also gave the same results.



3a



3b



3c

Figure 1 shows the AM 1 structure of the cycloadduct **1**. The carbon–carbon bond distance (1.613 Å) of the 1,3-diphenyl-2-pyrazoline skeleton of **1** is close to that (1.521 Å) of the X-ray structure[8] of **2**. The 1,2-addition at a 6,6-junction of C_{60} leading to **3a** is also evidenced by the agreement between the number of observed ^{13}C NMR signals (41) and the theoretical value for the C_s struc-

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[3] Typical examples are as follows: (a) Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K. C.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T.; Rickborn, B.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 1594. (b) Schlueter, J. A.; Seaman, J. M.; Taha, S.; Cohen, H.; Lykke, K. R.; Wang, H. H.; Williams, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 972. (c) Komatsu, K.; Murata, Y.; Sugita, N.; Takeuchi, K.; Wan, T. S. M. *Tetrahedron Lett.* **1993**, *34*, 8473. (d) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc.* **1993**, *115*, 344. (e) Belik, P,; Gügel, A.; Spickermann, J.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 78. (f) Khan, S. I.; Oliver, A. M.; Paddon-Row, M. N.; Rubin, Y. *J. Am. Chem. Soc.* **1993**, *115*, 4919. (g) Ohno, M.; Azuma, T.; Eguchi, S. *Chem. Lett.* **1993**, 1833. (h) Isaacs, L.; Haldimann, R. F.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2339. (i) Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 4093.

[4] Mathews et al. have reported that reaction of C_{60} with 1,3-diphenyl nitrilimine affords only the diadducts,[5] which is quite different from our results as shown in this paper.

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[6] Only typical examples are shown here: (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* **1991**, *254*, 1186. (b) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *J. Am. Chem. Soc.* **1992**, *114*, 7300. (c) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301. (d) Shi, S.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656. (e) Vasella, A.; Uhlmann, P.; Waldraff, C. A. A.; Diederich, F.; Thilgen, C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1388. (f) Smith, A. B., III; Strogin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829. (g) Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479 and references cited in these papers.

[7] (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

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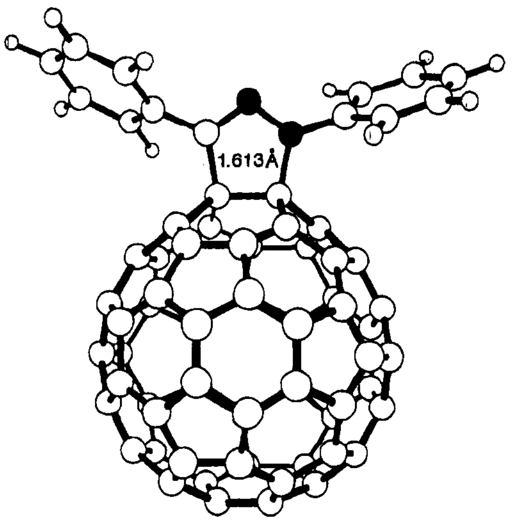

Figure 1. AM 1 structure of the cycloadduct **1** (●, N atom, ○, C atom; ○, H atom).

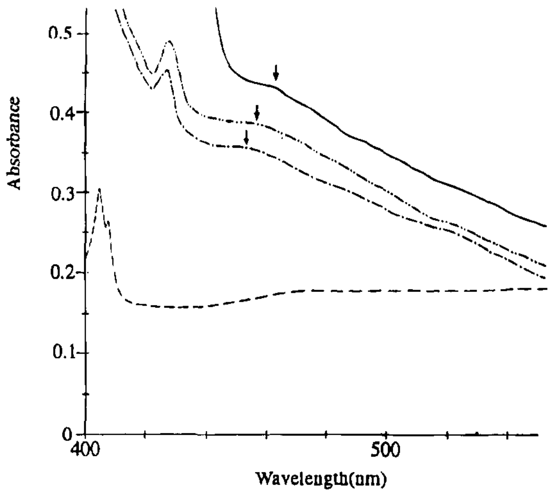

Figure 2. Charge transfer band observed for **1** (concentration 18.2 mg in 100 mL of solvent, at room temperature). Solvent: cyclohexane (– • –), methylene chloride (– •• –), and carbon disulfide (—). Spectrum (- - -) is due to the same concentration of C_{60} in cyclohexane.

Table 1. Redox Potential for 1 and C_{60} (V vs Ferrocene/ Ferrocenium in Benzonitorile with 0.05 M Bu_4NBF_4) at 20 °C

compd	$E_{red}{}^1$	$E_{red}{}^2$	$E_{red}{}^3$
C_{60}	$-0.94E_{1/2}$	$-1.37E_{1/2}$	$-1.86E_{1/2}$
1	$-1.17E_{1/2}$	$-1.58E_{1/2}$	$-2.11E_{1/2}$

ture.[9,10] If the cycloadduct has the **3b** structure (C_1 symmetry) the observed signals should be 73. Further support for the assigned structure derives from the ^{15}N NMR spectra for the 1-^{15}N-labeling compounds of **1**, **2** and 1,3-diphenyl-2-pyrazole (**4**) which we prepared starting from ^{15}*N*-aniline. The ^{15}N chemical shift (−221.95 ppm, shift from nitromethane as the standard) for **1** is very close to that of **2** (−228.22) and not to that of **4** (−164.47, a model for the aromatic system) indicating that **1** has a 2-pyrazoline ring.

From the 500 MHz ^{1}H NMR chemical shifts for **1** and **2** (see supporting information), it is shown that each signal of **1** is shifted to lower field than the corresponding signal of **2**. Of those, the low-field shift for the *ortho* protons, in particular, those for *N*-phenyl ($\Delta\delta$ 0.79), is remarkable. Since (1) this low-field shift increases markedly by replacing the C-phenyl of **1** with *C*-*tert*-butyl[11] ($\Delta\delta$ 1.79 *for o*-H, 1.28 *for m*-H, 1.52 *for p*-H) and (2) the shortest distance between the C_{60} sphere of **1** and the benzene ring is 3.15–3.19 Å, the remarkable low-field shift for the *ortho* protons seems to suggest an intramolecular CT interaction between the benzene ring (in particular, *N*-phenyl) and the C_{60} sphere (π acceptor).[12] This was proved by the observation of the CT band at around 470 nm (log ϵ 3.2) which was shifted toward longer wavelength with increasing solvent polarizability as shown in Figure 2. This is a first observation of definite intramolecular charge transfer in C_{60} derivatives, although the intermolecular CT band between C_{60} and benzene derivatives (e.g., λ_{max} around 450 nm for methoxy benzenes[1] and 600 nm for *N,N*-diethylaniline[2]) is already reported. In accord with this observation, the reduction potential ($E_{1/2}$) of **1** was shifted to the negative side by around 0.2 V compared with those of C_{60} as demonstrated in Table 1.

A rationale for the intramolecular charge transfer is given by the large HOMO π electron distribution[12] for the pyrazoline π part (80.6%), in particular for the *N*-phenyl (45.7%) of **1**. Thus, it is concluded that the *N*-phenyl group interacts more strongly with the C_{60} sphere than the *C*-phenyl group does in the competitive intramolecular CT interaction in **1**.

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Supporting Information Available: Experimental procedure and characterization data (6 pages).

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[9] Since the energy barrier between both isomers due to the direction of the *N*-phenyl group is only 2.96 kcal/mol (AM1), **3a** seems to have C_s symmetry at room temperature.

[10] The observed 41 signals in the 125 MHz ^{13}C NMR spectra are shown in the supporting information. Those six signals appearing between δ 124 and 130 ppm are assigned to 10 carbons of both phenyl CH groups from $^{13}C-^{1}H$ COSY spectrum. The 33 signals appearing between δ 130 and 150 ppm are assigned to (1) two phenyl carbons without hydrogen, (2) one sp^2 carbon of the pyrazoline ring, and (3) 58 sp^2 carbons of the C_{60} skeleton. The two signals appearing at δ 82.34 and 92.52 ppm can be assigned to the sp^3 carbon formed by the cycloaddition.

[11] Preparation and properties of 1-*tert*-butyl-3-phenyl-2-pyrazoline ring-fused C_{60} will be reported elsewhere.

[12] From AM1 calculations the electron affinity of **1** is very close to that of C_{60} (2.95eV) indicating **1** to be a strong electron acceptor.