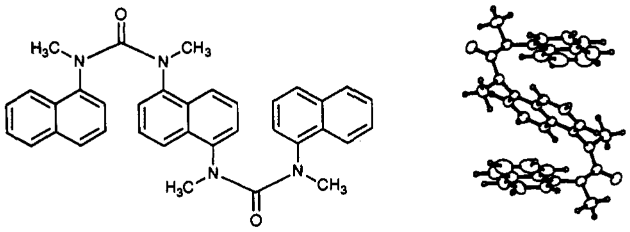

Figure 4. Structure and an ORTEP view of **6**.

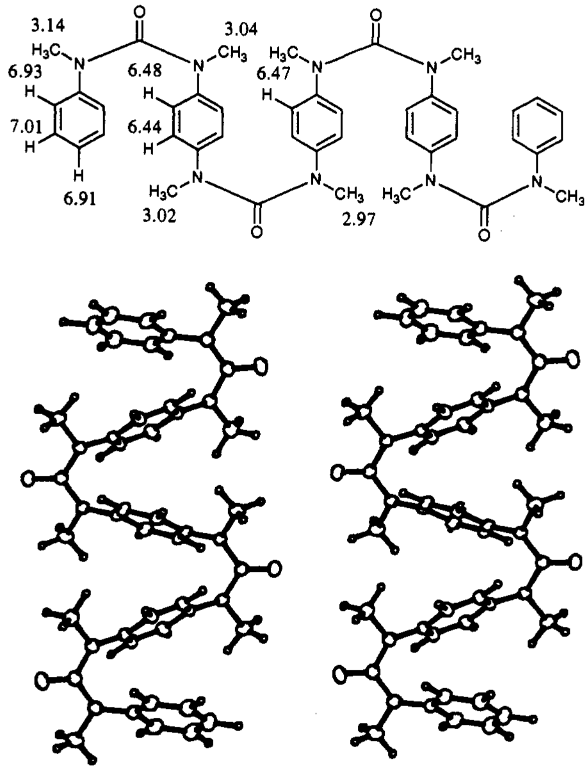

Figure 5. Structure and an ORTEP stereoview of **7**.

field chemical shift of the ortho protons may reflect the combined anisotropic effects of the central benzene ring and an adjacent aniline ring.

Another interesting example of stereochemical switching was found during the N-methylation of ureas. Aromatic ureas exist in transoid structures.[6] However, the cis preference of *N*-methyl-*N*,*N'*-diphenylureas[7] and the bis-cis preference of *N*,*N'*-dimethyl-*N*,*N'*-diphenylurea[8] also seem to be intrinsic. Two examples, *N*,*N'*,*N''*,*N'''*-tetramethyl-1,5-bis(1-naphthylureido)naphthalene (**6**) and an *N*-methyl derivative of a poly(phenyleneureido)benzene (**7**) may be of interest.

The bis-cis conformation of the ureido structure of **6** is retained in both the ureido structures (Figure 4). An NMR study on **6** was not very informative, but definitely showed the presence of at least partial aromatic-aromatic interactions. The structure of the five-layered urea derivative (**7**) is beautifully shown in Figure 5. The angle between the first and the second benzene-ring planes is 38.5° and that between the second and the third ring planes is 46.7°. The angle between the first and the third is 12.1°, close to parallel, and the distance between the parallel second and fourth planes is 7.29 Å. The distances between aromatic carbon atoms bearing a nitrogen atom are 3.31 Å (the first and second) and 2.96 Å (the second and third). The solution stereochemistry is considered to be quite similar to the crystal structure: the NMR chemical shifts presented in the structure for the terminal aromatic rings are close to those of *N*,*N'*-dimethyl-*N*,*N'*-diphenylurea,[7] and the chemical shifts for the second and third aromatic rings are very close to those of the central ring of *N*,*N'*,*N''*-trimethyl-1,4-bis(phenylureido)benzene, which also exists in a similar layered structure.[8] Nuclear Overhauser effects are also consistent with the assigned solution structure. In this system, some aromatic interactions (close to parallel benzene-benzene interactions)[5] probably exist, and such long-range aromatic-aromatic interactions may constitute a new area of chemical research.

The examples shown here are only fundamental compounds, but they demonstrate the usefulness of the *N*-methylamide moiety in constructing molecular structures of various types. The ease of introduction of the *N*-methylamide moiety into molecules makes this strategy attractive in molecular design.

Supplementary Material Available: X-ray crystallographic details for compounds **3-7** including the atom-numbering scheme and tables of bond lengths and angles, atomic coordinates, and anisotropic thermal parameters (20 pages); listing of observed and calculated structure factors for compounds **3-7** (33 pages). Ordering information is given on any current masthead page.

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Fluorinated Fullerenes

H. Selig,[*,†] C. Lifshitz,[†] T. Peres,[†] J. E. Fischer,[‖,‡]
A. R. McGhie,[‡] W. J. Romanow,[‡] J. P. McCauley, Jr.,[‡,§] and
A. B. Smith, III[‡,§]

Institute of Chemistry, Hebrew University
Jerusalem, Israel
Department of Materials Science &
Engineering, Laboratory for Research on the
Structure of Matter, and
Department of Chemistry, University of Pennsylvania,
Philadelphia, Pennsylvania 19104

Received April 22, 1991

The fullerenes, C_{60} and C_{70}, have received much attention recently.[1-4] They are now considered to be a new allotropic form of carbon. All the carbon atoms in C_{60} are equivalent. Therefore, one might expect a fully fluorinated molecule of stoichiometry $C_{60}F_{60}$. Such a molecule, as well as $C_{60}H_{60}$, has indeed been calculated to be stable.[5] We have undertaken the fluorination of powdered materials containing C_{60} and C_{70} in various ratios.

Starting materials were prepared via standard techniques: soot production by "burning" graphite rods in a 300-Torr helium atmosphere and Soxhlet extraction in boiling toluene, followed in some cases by liquid chromatography in hexanes on neutral alumina.[6] The resulting powders were dried in flowing nitrogen at 400 °C to drive off all traces of solvent. Most experiments were carried out on unpurified extract containing about 10% C_{70}; mass spectra were also measured on a 90% C_{70} sample.

[†] Institute of Chemistry, Hebrew University.

[‖] Department of Materials Science & Engineering, University of Pennsylvania.

[‡] Laboratory for Research on the Structure of Matter, University of Pennsylvania.

[§] Department of Chemistry, University of Pennsylvania.

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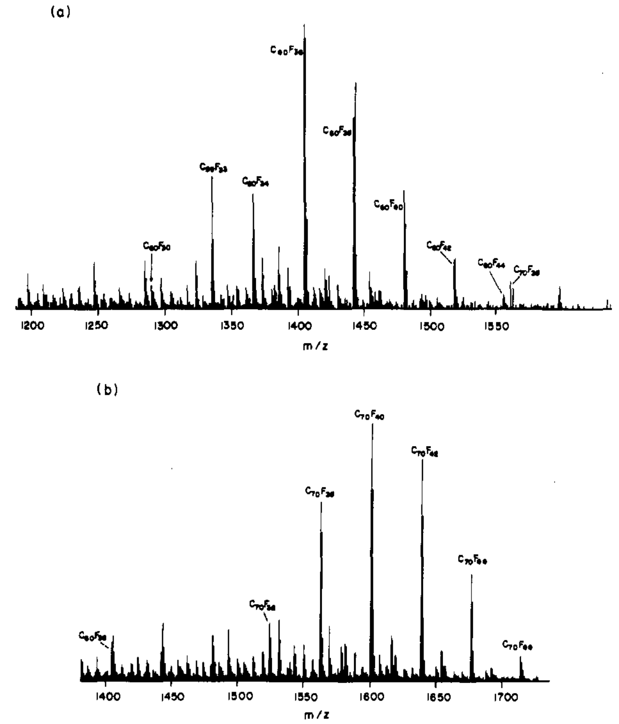

Figure 1. Mass spectra of fluorinated fullerenes: (a) a C_{60}-rich sample at a probe temperature of 200 °C; (b) a C_{70}-rich sample at a probe temperature of 300 °C.

Fluorinations were performed on a Sartorius magnetic suspension balance, Model 4201. This allowed us to monitor in situ weight uptake (±0.1 mg) while the sample was exposed to a fluorine pressure of several hundred Torr. Usually fluorine uptake was almost complete within a few minutes and then continued very slowly for up to 20 h to constant weight. Weight uptakes were measured ex situ with 0.01-mg precision. Results varied from sample to sample but usually indicated $F/C_{60} > 30$. A 9.22-mg sample of pure C_{60} gave a weight increase upon fluorination of 9.24 mg corresponding to $F/C_{60} = 38.0 \pm 0.1$. Small amounts of pure C_{60} were fluorinated separately in an IR cell. By following the absorption at 1283 cm^{-1}, we could see that small amounts of CF_4 were slowly liberated. Thus, the weight uptakes represent lower limits. A few samples were analyzed for fluorine content by igniting weighed portions in oxygen in a Schoniger flask and titrating with $La(NO_3)_3$. The results agree roughly with the weight uptake measurements, although usually showing somewhat lower fluorine content, a problem generally encountered with molecules of high fluorine content.

Mass spectra were run on a ZAB-2F (VG-Analytical) double-focusing instrument of reverse geometry. The samples were introduced into the mass spectrometer by using the direct-insertion probe, which was heated up to 400 °C. The EI mass spectrometry conditions were as follows: electron-ionizing energy, 70 eV; emission current, 1 mA; source temperature, 250 °C; and resolution, 2000 (10% valley definition). Typical mass spectra are presented in Figure 1. Part a shows the spectrum for a C_{60}-rich sample at a probe temperature of 200 °C, and part b shows the spectrum for a C_{70}-rich sample at a probe temperature of 300 °C. The spectra show mass groups with intervals of 2F = 38. The most intense peak in fluorinated C_{60} occurs at $m/z = 1404$, indicating a particularly stable molecule, $C_{60}F_{36}$, analogous to the product of the Birch reduction, $C_{60}H_{36}$.[3] MIKE (mass analyzed ion kinetic energy) and CAD (collisionally activated dissociation) spectra were run on several of the major ions, including $C_{60}F_{36}^+$, $C_{60}F_{38}^+$, $C_{60}F_{40}^+$, $C_{60}F_{42}^+$, and $C_{60}F_{44}^+$, in order to find out whether some of these ions are due to fragmentation. No F_2 elimination was observed from any of these ions, clearly indicating that these are all parent ions of the corresponding neutral fluorinated compounds ($C_{60}F_{36}$, $C_{60}F_{38}$, etc.). The characteristic fragmentations of these ions are $F^\bullet$ and $CF_3^\bullet$ and $C_2F_5^\bullet$ eliminations. As a result, the ion $C_{59}F_{33}^+$ in the mass spectrum (Figure 1a) is a major fragment from $C_{60}F_{36}^+$ due to $CF_3^\bullet$ loss. At higher probe temperature (400 °C), the C_{60}-rich sample gave peaks at $C_{60}F_{46}^+$, $C_{60}F_{48}^+$, $C_{60}F_{50}^+$, and $C_{60}F_{52}^+$. The most intense peak in the C_{70} spectrum (Figure 1b) is at $m/z = 1600$, corresponding to $C_{70}F_{40}^+$, although higher fluorinated C_{70} ions up to $C_{70}F_{46}^+$ are clearly present.

Infrared spectra show a strong, broad absorption at 1165 cm^{-1} characteristic of a C–F stretch with partial ionic character (the C–F absorption in covalent graphite fluoride occurs at 1215 cm^{-1}).[7] A TGA experiment on a C_{60}-rich sample showed decomposition at 320 °C; a major constituent in the downstream mass spectrum was CO_2, suggesting that the relatively poor thermal stability is due to air exposure of the product. The fluorinated material is brown to tan colored. Most of the products appeared inhomogeneous under the microscope, suggesting the presence of several phases, possibly with different degrees of fluorination. In a few cases, small amounts of a yellow-white material were observed.

After fluorination, an X-ray powder profile exhibits only a few broad peaks characteristic of a liquid or glass with short-range positional correlations and no long-range order. The starting material is highly crystalline.[8] In monatomic glasses the near-neighbor distance is simply and directly related to the position of the first diffuse scattering maximum. No such relationship exists for disordered molecular solids. However, the fact that the first diffuse maximum after fluorination occurs at about $2\theta = 9°$ is consistent with an increased near-neighbor intermolecular distance relative to the pristine structure. An amorphous structure is also consistent with differential scanning calorimetry, which shows a broad glass transition near 20 °C and no first-order transitions in the range −140 to 200 °C.

Acknowledgment. This research was supported by the German–Israeli Foundation for Research and Development and by the National Science Foundation Materials Research Laboratory Program, Grant No. DMR88-19885.

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Unusually Stable γ-Lactone Ring Fused Norcaradienes from Intramolecular Cyclization of Vinylcarbenes

Shigeo Kohmoto,*,† Teruyuki Kawatsuji,† Koreharu Ogata,‡
Makoto Yamamoto,† and Kazutoshi Yamada†

*Department of Materials Science, Faculty of
Engineering, Chiba University
1-33, Yayoi-cho, Chiba 260, Japan
Chemical Analysis Center, Chiba University
1-33, Yayoi-cho, Chiba 260, Japan*

Received December 17, 1990
Revised Manuscript Received May 16, 1991

Intermolecular carbenoids addition to benzene ring is the most commonly used method to prepare norcaradienes.[1] But an intramolecular version of this reaction has never been successful in affording stable norcaradienes of tricyclic structures. Since 1970, intramolecular cyclization of aryl diazoketones has been

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† Department of Materials Science, Faculty of Engineering, Chiba University.

‡ Chemical Analysis Center, Chiba University.

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