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Reaction of Buckminsterfullerene with 1,3-Diphenylnitrilimine : Synthesis of Pyrazoline Derivatives of Fullerene

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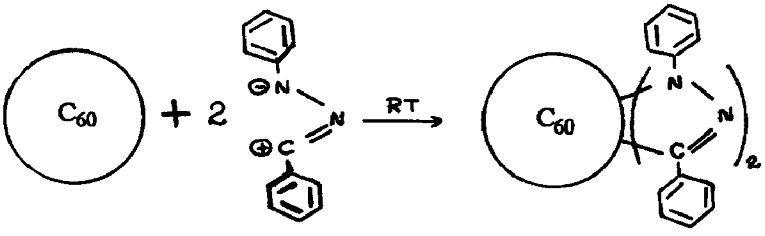
Abstract : 1,3-diphenylnitrilimine generated in situ undergoes 1,3-dipolar cycloaddition with C_{60} to form a diadduct which is characterised by FAB mass spectrum and other spectroscopic techniques.

Key words : Fullerene, dipolar, cycloaddition, nitrilimine

The discovery of buckminsterfullerene has attracted worldwide attention as a result of its fascinating properties[1]. C_{60} with an extended array of pi electrons act as dienophile with a strong tendency for cycloaddition reaction and this has been confirmed in a number of studies[2,3]. C_{60} was found to add a few dipoles such as nitrile oxides[4], azides[5] and diazomethane[6], wherein C_{60} is used as a dipolarophile. In an attempt to widen the scope of such reactions, we report here our preliminary results on the reaction of C_{60} with 1,3-diphenylnitrilimine(DPNI).



1,3-diphenylnitrilimine diadduct

Scheme 1

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A solution of C_{60} (54 mg, 0.75 mmol) in dry benzene (50 ml) was stirred with benzhydrazidoyl chloride (35 mg, 1.5 m mol) in the presence of triethylamine at room temperature. The reaction was allowed to proceed for 10 days after which the triethylamine hydrochloride was filtered and the benzene solution washed several times with water and dried over $MgSO_4$. The solvent was removed by vacuum evaporation and the residue (65 mg, 78 %) was analysed by TLC. The TLC analysis indicated the absence of starting materials.

The IR spectrum (Fig. 1) of the product showed a strong peak at 1597 cm^{-1} characteristic of C = N group. There is a marked change in the IR pattern from that of pure C_{60}.

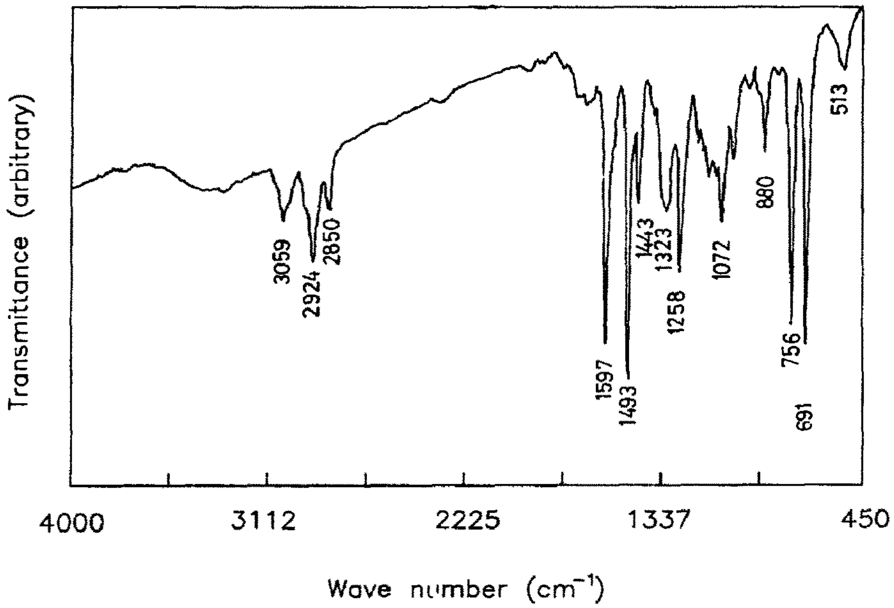

Fig.1 : Infrared spectrum of the reaction product in KBr using a Digilab FTS 15/90 FTIR Spectrometer

FAB mass spectrum (Fig. 2) of the product using the m-nitrobenzyl alcohol as a matrix and an argon beam of 6 kV energy as the probe gave a moderately strong molecular ion peak at m/z 1109 (M^+ + H) indicating the formation of a diadduct (Scheme I) with a base peak at m/z 720 corresponding to C_{60}. Fragmentation of the DPNI adduct occurs by successive losses of DPNI ultimately restoring to C_{60} in the mass spectrum. Elemental analysis of the product also supported the formation of diadduct with 5.02 % nitrogen present in the product (5.05 % expected), while the carbon value was found to be lower than expected as reported by Suzuki et al[7].

^1H NMR spectrum of the product showed a complex multiplet between 7.20 to 7.60 ppm due to aromatic protons. In the ^{13}C-NMR spectrum, the chemical shift of all the carbons in C_{60} as well as aromatic carbons appeared in the fulleroid region between δ 110 - 150 ppm, the aromatic carbons

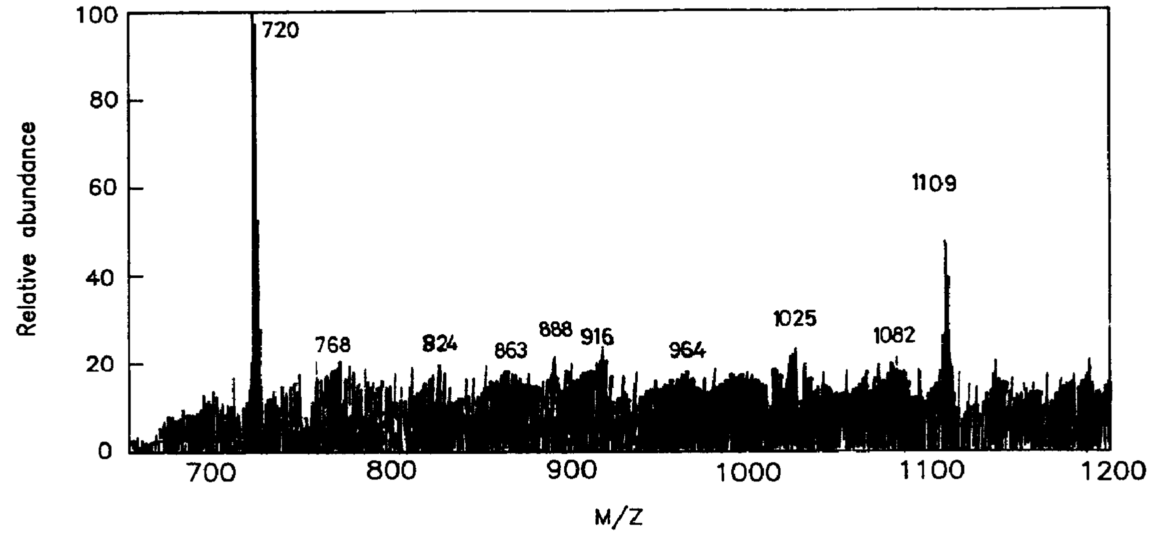

Fig.2 : Part of the FAB mass spectrum of the reaction product showing the diadduct using JEOL SX 102/DA 6000 Mass spectrometer with argon gas in m-nitrobenzylalcohol matrix

appearing at up-field (δ 110 - 130 ppm) while the sp^2 carbons of fullerene appeared at low field (δ 130 - 150 ppm). The double intensity lines corresponding to δ 116.15 and 124.04 ppm are assignable to sp^3 carbon atoms of the cycloadduct where the addition of 1,3- dipole takes place. The signals in the region of δ 115 - 140 ppm are well resolved[8] and the signals above δ 140 upto 150 ppm were found to be complex.

Based on the above information we conclude that a diadduct is formed by the reaction of C_{60} with 1,3-diphenylnitrilimine as represented in Scheme 1.

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8. ^{13}C NMR data (400 MHz Bruker WM-400, $CDCl_3$ + 0.02 M $Cr(acac)_3$): δ 116.15, 124.04, 125.58, 126.15, 126.35, 126.54, 126.73, 126.92, 127.11, 127.88, 128.27, 128.46, 129.23, 131.15, 131.35, 131.54, 131.92, 132.31, 132.50, 135.58, 139.42 ppm.

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