The Transannular Bond in [5,6]-NCO_2R-bridged Monoadducts of [60]Fullerene is Open

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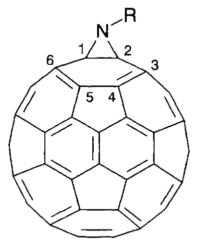
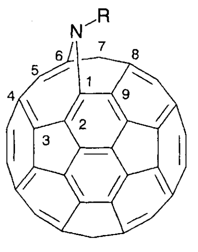
^{13}C NMR investigations of [5,6]-NCO_2R- and [5,6]-$^{15}NCO_2R$-bridged monoadducts of [60]fullerene obtained by the thermal reaction of [60]fullerene with azidoformates show that the transannular bond is open.

It is well established that monomethano- or monoimino-[60]fullerenes are either [6,6]-bridged compounds with a closed or [5,6]-bridged compounds with an open transannular bond.[1–12] In these isomers the introduction of energetically unfavourable double bonds in five-membered rings is avoided, whereas hypothetical open [6,6]-bridged and closed [5,6]-bridged isomers require the introduction of three and two double bonds in five-membered rings respectively. However, in contrast to the expected generalisation of this principle, the isolation of closed [5,6]-iminobridged fullerenes has been claimed recently.[13] Here, we report independent investigations on these compounds, which prove that the transannular [5,6]-bonds are open.

Closed [6,6]-imino-bridged monoadducts of [60]fullerene can be obtained by [2 + 1] cycloadditions of nitrenes, which were generated *in situ* by α-elimination of *O*-4-nitrophenylsulfonylalkylhydroxamic acids[7] {side products}, by thermal N_2-elimination of azidoformates[6] {[5,6] side products} or photochemically from azidoformates[11] {no [5,6] side products}, whereas the open [5,6]-iminobridged isomers are accessible by [3 + 2] cycloadditions of alkyl azides followed by N_2-extrusion from the triazoline intermediates[4,5,8,9,10,12] {[6,6] side products}. The [5,6] side products obtained by the thermal reaction of the azidoformates N_3CO_2R (R = Et, Bu^t supermesityl) have been assigned as the first examples for closed [5,6]-bridged fullerene adducts.[13] This interpretation was based on the findings that: (i) these compounds are C_s-symmetric (^{13}C NMR); (ii) no 420 nm bands in the UV/VIS-spectra characteristic for [6,6]-isomers[5] are present and (iii) signals between δ 80 and 105 have been observed in ^{13}C NMR spectra, which were attributed to sp^3-C-atoms of the fullerene core bound to the imino-bridge. With the exception of these signals the reported spectroscopic data are fully consistent with open [5,6]-bridged structures.[4]



1a,b



2a,b

a R = CO_2Et
b R = CO_2Bu^t

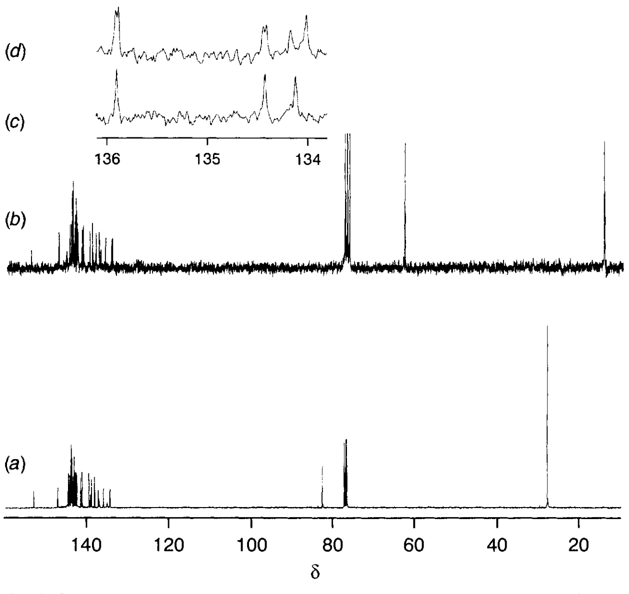


Fig. 1 ^{13}C NMR spectra (62.9 MHz, CS_2–10% $CDCl_3$, 25 °C) of (*a*) **2b**, (*b*) **2a** with the comparison of the 136–134 ppm regions of (*c*) **2a** and (*d*) ^{15}N-**2a** showing the $^1J_{C,N}$ coupling and the two $^2J_{C,N}$ couplings of the ^{15}N-iminobridge with the fullerene sp^2-C-atoms C-1, C-6 and C-2, C-5 and C-7, C-9 respectively

When we allowed a boiling solution of [60]fullerene in 1,1,2,2-tetrachloroethane to react with 1 equiv. of N_3CO_2Et (identical conditions to those used in ref. 13) we also obtained the [6,6]-isomer **1a** as the major product (27%) and the [5,6]-isomer **2a** as the minor product (2%); however, **2a** is the ring-open isomer. Compounds **1b** and **2b** are not easily accessible by this method since they readily undergo follow-up reactions to the NH-analogues.[14] The spectroscopic properties† of **2a** are the same as those reported for the [5,6]-adduct in ref. 13, except that we do not see a signal at δ 80.4 in the ^{13}C NMR spectrum. The only signals in the sp^3-region are due to the ethyl groups in **2a** (Fig. 1). The comparison of the ^{13}C NMR spectra of **2a** with those of 100% ^{15}N-labelled **2a** proves unambiguously that the transannular [5,6]-bond is open (Fig. 1). The $^1J_{C,N}$ coupling of 9.5 Hz at δ 134.10 is due to the bridging nitrogen with the sp^2-C-atoms, C-1 and C′-6. The doublets at δ 135.90 and 134.43 are caused by $^2J_{C,N}$ couplings with C-2, C-5 and C-7, C-9 respectively.

An important pathway leading to **2a** should be [3 + 2] cycloaddition of N_3CO_2Et and N_2 extrusion of the initially formed triazolines. This mechanism is the major pathway for the reaction of [60]fullerene with alkyl azides.[5] To prove this hypothesis we allowed [60]fullerene to react with 1 equiv. of $N_3CO_2Bu^t$ in a concentrated 1-chloronaphthalene solution at 60 °C, which are typical conditions for the formation of triazolines.[5] Upon dilution of the reaction mixture with toluene to a tenfold volume and heating to 120 °C compounds **1b** and **2b** are formed from the more polar triazoline intermediate (TLC control). The ratio of the yields of the [6,6]- and [5,6]-isomers is reversed (3% **1b**, 16% **2b**) compared to the direct thermal treatment of [60]fullerene with N_3CO_2Et, where the [2 + 1] cycloaddition of stabilised carbonyl nitrenes leading predominantly to [6,6]-adducts like **1** is the preferred process.

The spectroscopic properties† of the open [5,6]-bridged **2b** are comparable to those of **2a** (Fig. 1). The only signals for sp^3-atoms detected by ^{13}C NMR spectroscopy are due to the quaternary (δ 82.63) and the primary (δ 27.95) C-atoms of the *tert*-butyl groups, We have never found a [5,6]-iminobridged adduct with a closed transannular bond in any of our reaction products.

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Footnote

† *Selected data* for ^{15}N-**2a**: ^{13}C NMR (62.9 MHz, CS_2–10% $CDCl_3$, 25 °C): δ 153.97 (d, $^1J_{C,N}$ 26.2 Hz), 147.14, 145.27, 144.58, 144.21, 144.13, 143.97, 143.91, 143.88, 143.69, 143.34, 143.16, 142.90, 142.76, 142.68, 142.60, 142.49, 141.50, 141.18, 139.53, 138.98, 138.30, 138.20, 137.41, 137.06, 135.90 (d, $^2J_{C,N}$ 1.0 Hz), 134.43 (d, $^2J_{C,N}$ 2.1 Hz), 134.10 (d, $^1J_{C,N}$ 9.5 Hz), 62.97, 14.64; ^{1}H NMR (250 MHz, CS_2–10% $CDCl_3$, 25 °C): δ 1.44 (t, *J* 7.1 Hz), 4.43 (q, *J* 7.1 Hz); λ_{max}/nm (CH_2Cl_2) 260, 329, 428 (sh), 414 (sh), 502, 600; FAB MS (*m*-nitrobenzyl alcohol, NBA) (M^+) *m*/*z* 808. For **2b**: ^{13}C NMR (62.9 MHz, CS_2–10% $CDCl_3$, 25 °C): δ 153.05, 147.15, 144.49, 144.22, 144.10, 143.92, 143.84, 143.73, 143.65, 143.62, 143.29, 143.11, 142.93, 142.86, 142.62, 142.56, 142.46, 141.52, 141.11, 139.44, 139.02, 138.85, 138.21, 138.15, 137.26, 136.98, 135.96, 134.99, 134.38, 82.63, 27.95; ^{1}H NMR (250 MHz, CS_2–10% $CDCl_3$, 25 °C): δ 1.62 (s); λ_{max}/nm (CH_2Cl_2) 261, 330, 413 (sh), 429 (sh), 509, 600 (sh); FBMS (NBA) (M^+) *m*/*z* 835.

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