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N-Unsubstituted fulleropyrrolidine derivatives: reinvestigation, structural reassignment and new insight

Guan-Wu Wang *, Zhi-Guo Tian

Hefei National Laboratory for Physical Sciences at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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ABSTRACT

The reaction of [60]fullerene with α-amino acids and aldehydes affording N-unsubstituted 2,5-disubstituted fulleropyrrolidines was reinvestigated. The previously reported stereochemistry should be reassigned. A reversible interconversion between the cis and trans stereoisomers of fulleropyrrolidines was observed for the first time.

1,3-Dipolar cycloaddition reaction is one of the most effective and convenient methods to functionalize fullerenes. Prato and co-workers[1] were the first to establish such 1,3-dipolar cycloaddition protocol by addition of azomethine ylides to [60]fullerene (C_{60}). Then reactions of C_{60} with a series of azomethine ylides generated from various α-amino acid derivatives and different aldehydes, known as Prato reaction, were successfully employed to prepare fulleropyrrolidine derivatives.[2] Among them, much fewer examples of 2,5-disubstituted fulleropyrrolidines consisting of both cis and trans isomers have been reported.[3–5] N-Unsubstituted 2,5-disubstituted fulleropyrrolidines are important precursors for further functionalizations.[4b,6]

Structure misassignments of fullerene products caused confusion, yet happened occasionally in the literature. For example, the reported [5,6]-closed adducts generated from the reaction of C_{60} with azidoformates[7] were later reassigned as [5,6]-open adducts,[8] and the previously reported [6,6]-open adduct[9] produced from the reaction of C_{60} with a nitrile ylide proved to be a [6,6]-closed adduct.[10]

Wilson and co-workers described the reaction of C_{60} with amino acids and aldehydes affording both cis and trans isomers of N-unsubstituted 2,5-disubstituted fulleropyrrolidines.[4a] The assignment of the cis and trans isomers was solely based on the ^{1}H NMR chemical shifts of the pyrrolidine methine protons. Their criterion was based on the assumption that *the signals for the* cis*-isomers always appear further downfield than the corresponding signals for the* trans*-isomers.*[4a] This assignment was questioned by Komori et al.[11] and was contradictory to the chemical shift trend for the pyrrolidine methine protons of other N-unsubstituted 2,5-disubstituted fulleropyrrolidines.[3,11] Wilson and co-workers attempted to reclaim their assignment by treating the cis and trans isomers of fulleropyrrolidines with a chiral isocyanate and resolving the resulting diastereoisomers. However, the demonstrated example consisting of a 1:1 cis/trans mixture of 2,5-dimethylfulleropyrrolidine was not appropriate to correlate with the ^{1}H NMR chemical shifts of the pyrrolidine methine protons.[12] We believe that the cis and trans isomers can be unequivocally assigned based on their NOESY and ^{13}C NMR spectra, which were not measured in Wilson's work.[4] Another interesting phenomenon in Wilson's work lied in the stereoselectivity: *cis* isomer was the major or even exclusive product in some cases while reversed stereoselectivity was observed in other cases. In order to avoid the confusion caused by misleading structure assignment and to better understand stereoselectivity, herein we reinvestigate a few selected reactions reported in Wilson's work, and correct the misassignments for the cis and trans isomers of fulleropyrrolidines. Furthermore, we also disclose the intriguing interconversion of the cis and trans isomers.

The reaction of C_{60} with alanine and benzaldehyde, that with alanine and acetaldehyde, that with phenylalanine and phenylacetaldehyde, and that with phenylglycine and benzaldehyde were chosen for our investigation. The first reaction afforded isomers of unsymmetrical fulleropyrrolidines (*cis*-**1a** and *trans*-**1a**), the latter three gave isomers of symmetrical fulleropyrrolidines (*cis*-**1b** and *trans*-**1b**, *cis*-**1c** and *trans*-**1c**, *cis*-**1d** and *trans*-**1d**, respectively) (Scheme 1).

* Corresponding author. Tel./fax: +86 551 360 7864.
E-mail address: gwang@ustc.edu.cn (G.-W. Wang).

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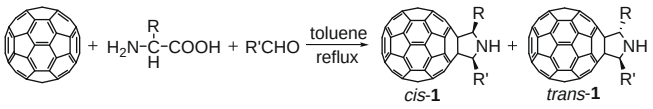


1a: R = CH_3, R' = Ph; **1b**: R = R' = CH_3; **1c**: R = R' = CH_2Ph; **1d**: R = R' = Ph

Scheme 1. The cycloaddition reaction of C_{60} with azomethine ylides generated in situ from α-amino acids with aldehydes.

A typical reaction was carried out by treating 72.0 mg of C_{60} with 2 equiv of an amino acid and 5 equiv of an aldehyde in refluxing toluene for the designated time under a nitrogen atmosphere. After usual workup, the products along with recovered C_{60} were obtained by flash column chromatography on a silica gel column. It should be pointed out that we successfully achieved the separation of individual cis and trans isomers of both **1b** and **1c** by employing a very long silica gel column.[13] The reaction times and product yields along with recovered C_{60} are listed in Table 1.

The cis and trans isomers of **1a**, **1b**, **1c**, and **1d** were unambiguously assigned based on their MS, ^{1}H NMR, ^{13}C NMR, IR, UV–vis, and NOESY spectra.[14] For the unsymmetrical fulleropyrrolidine **1a**, which has a C_1 symmetry, the stereochemistry could not be deduced from the ^{13}C NMR spectra, but could be determined by the NOESY spectra. The NOESY spectrum of *trans*-**1a** lacked the cross peak between the two methine protons, but clearly showed the cross peak between either of the methine protons and the methyl protons (Fig. 1), unequivocally proved the assigned structure. For

Table 1
Yields and conditions for the cycloaddition reactions of C_{60} with azomethine ylides in situ generated from α-amino acids with aldehydes

Entry	R_1	R_2	Reaction time (h)	Yield (%)		Recovered C_{60}
				Cis isomer	Trans isomer	
1	CH_3	Ph	9	15	19	52
2[a]	CH_3	CH_3	27	5	21	67
3	CH_2Ph	CH_2Ph	3	6	32	30
4	Ph	Ph	14	32	—	59

[a] Repeated separation by column chromatography was required to get pure isomer.

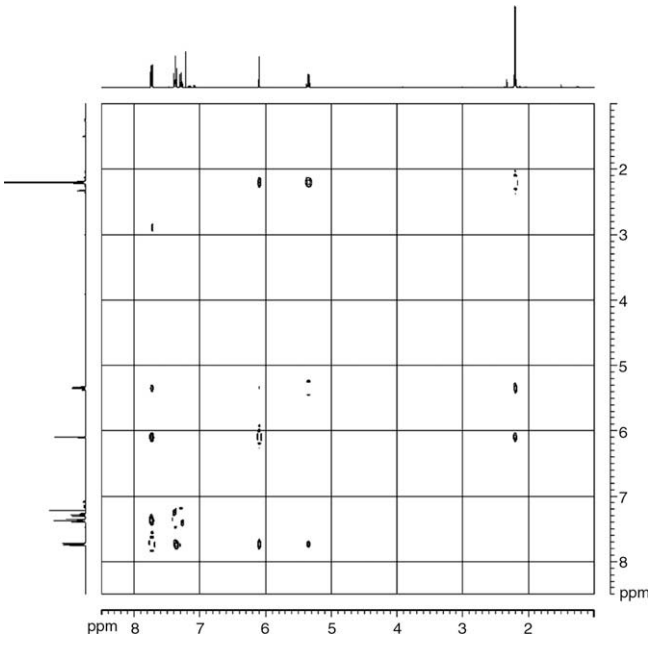


Figure 1. NOESY spectrum of *trans*-**1a**.

Table 2
The ^{1}H NMR chemical shifts for the methine protons on the pyrrolidine ring of **1a–d**

Entry	Compound	Cis isomer	Trans isomer
1	**1a**	5.80, 4.96	6.10, 5.35
2	**1b**	4.80	5.07
3	**1c**	4.71	5.07
4	**1d**	5.96	—

symmetrical fulleropyrrolidines **1b–d**, the cis isomers with C_s symmetry should theoretically give 32 peaks including 4 half-intensity ones (corresponding to 1C), while the trans isomers with C_2 symmetry should exhibit 30 peaks with equal intensity. Experimentally, half-intensity peaks were observed only in the ^{13}C NMR spectra of cis isomers of fulleropyrrolidines **1b–d**, confirming our assigned stereochemistry.

After the molecular structures including stereochemistries of fulleropyrrolidines **1a–d** had been unequivocally assigned, the ^{1}H NMR spectra of their cis and trans isomers were compared. The chemical shifts for the pyrrolidine methine protons of fulleropyrrolidines **1a–d** are listed in Table 2. As seen from Table 2, the signals for the cis isomers were shifted upfield by 0.27–0.39 ppm relative to those for the trans isomers. The same phenomenon could also be found in other reported fulleropyrrolidines.[3,11,15] Therefore, we conclude that Wilson's structure assignments[4] were incorrect and should be reassigned. The previously assigned cis and trans isomers[4] should be reassigned as trans and cis isomers, respectively. Accordingly, other structure assignments[5,6a] based on Wilson's criterion were most likely misassigned.

Another issue that attracted our attention in Wilson's work is the isomeric distribution. The cis isomer was reported to be the major product for **1a** and **1c**,[4a,16] while a 1:1 cis/trans isomeric mixture was obtained for **1b**.[4b] However, the trans isomer was the major product for **1a**, **1b**, and **1c** in our case. Through our extensive investigation on these reactions, we found that the main product was heavily dependent on the reaction conditions. As an example, when the reaction of C_{60} with alanine and benzaldehyde affording **1a** was extended from 9 h to 21 h in toluene at 110 °C, the major product was changed to the cis isomer. The yields for the *cis*-**1a** and *trans*-**1a** isomers were 28% and 15%, respectively. We surmised that this unusual behavior might result from the conversion between the *trans*-**1a** and *cis*-**1a** isomers. To confirm our hypothesis, pure *cis*-**1a** (10 mg) and *trans*-**1a** (10 mg) were separately dissolved in toluene (15 mL) and heated to 110 °C for 24 h under a nitrogen atmosphere. Unexpectedly, the same isomeric ratio (cis/trans = 71:29) was observed for both isomers. Obviously, the interconversion between *trans*-**1a** and *cis*-**1a** isomers existed an equilibration in refluxing toluene. It is noteworthy that *trans*-**1a** could be converted to *cis*-**1a** even at room temperature. Stirring *trans*-**1a** (10.0 mg) at ambient temperature in 1 mL of carbon disulfide/dimethyl sulfoxide (v/v, 5:1) for 24 h led to a mixture with a cis/trans ratio of 57:43. Unlike product **1a**, the conversion of **1b** and **1c** was very sluggish in refluxing toluene. To accelerate the conversion *o*-dichlorobenzene (ODCB) was employed as the solvent and the reaction temperature was elevated. Multi-adducts of C_{60} were obtained when the cycloaddition reaction was conducted with longer reaction time in refluxing toluene or ODCB. Therefore, the isomeric mixture of **1b** and **1c** was first separated from the reaction mixture and then heated in refluxing ODCB. Fulleropyrrolidine **1b** with a cis/trans ratio of 21:79 was heated in refluxing ODCB for 12 h and gave an obvious change of the cis/trans ratio to 85:15; Similar procedure was carried out for adduct **1c** and gave the analogous change of the cis/trans ratio from 14:86 to 73:27 (Fig. 2). This observation showed that the trans isomer was the major product for the cycloaddition reaction affording **1a–c** in refluxing toluene with short-reaction time, but the cis iso-

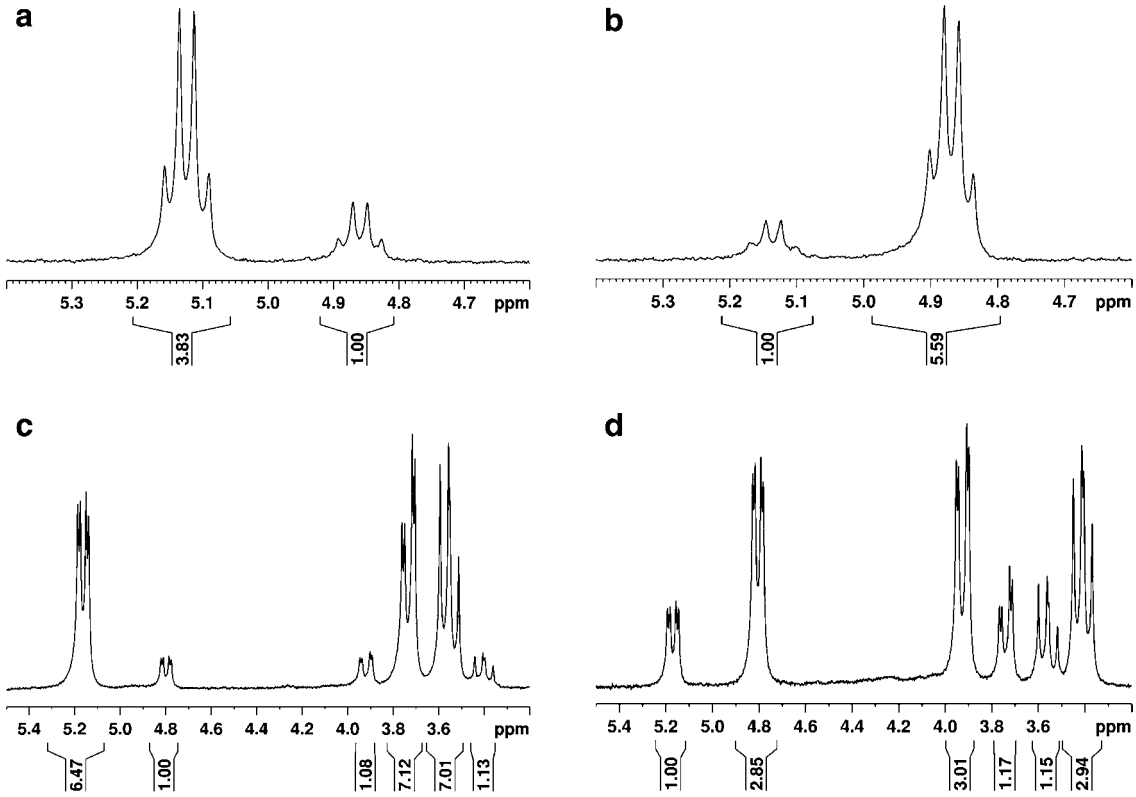
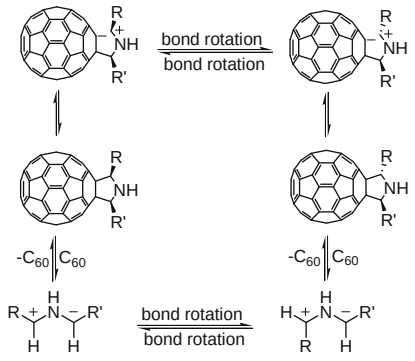


Figure 2. (a and c): Partial ^{1}H NMR spectra of **1b** and **1c** before heating. (b) and (d): Partial ^{1}H NMR spectra of **1b** and **1c** after heating in refluxing ODCB for 12 h.

mer became the major adduct while the reaction time was extended or the reaction temperature was increased. Therefore, we conclude that the trans isomer was the kinetically preferred product, while the cis isomer was the thermodynamically preferred product. In sharp contrast with predominant formation of the trans isomer for **1a**–**c**, only cis isomer of **1d** was obtained (Table 1). No trans isomer of **1d** could be detected even at the early stage of the reaction. The formation of only cis isomer of **1d** probably results from the kinetic control. To our surprise, the cis isomer of **1d** could not be transformed to its trans isomer. Fulleropyrrolidine **1d** with two bulky phenyl substituents at C2 and C5 atoms might behave differently from **1a**–**c**, which bear two alkyl substituents or a combination of one aryl and one alkyl substituent.

Based on the above-mentioned results, the proposed mechanism for the interconversion between cis and trans isomers of fulleropyrrolidines is shown in Scheme 2.

The cis and trans isomers could be transformed to each other by (1) the cleavage of one C–C bond of the pyrrolidine ring to generate a zwitterion intermediate, followed by rotation and then reformation of the C–C bond; or (2) cycloelimination, bond rotation of the resulting azomethine ylide, and recyclization. The first mechanism is favorable for sterically less hindered groups and unfavorable for bulky groups on the pyrrolidine ring. The feasibility for the interconversion of **1a**–**c** and the reluctance of *cis*-**1d** to form its trans isomer under heating seem to support such a mechanism. However, the cycloelimination step in the second mechanism should also exist for **1d**. Different from the clean interconversion of **1a**–**c**, heating **1d** produced some C_{60} and multiadducts of C_{60}. Additional evidence for the cycloelimination came from the interconversion between the cis and trans isomers of the fulleropyrrolidine bearing two bulky ester groups at C2 and C5 atoms, which also released some C_{60} and multiadducts of C_{60}.



Scheme 2. Possible mechanism of the interconversion between trans isomer and cis isomer of fulleropyrrolidines.

In conclusion, four reactions of C_{60} with α-amino acids and aldehydes affording unsymmetrical and symmetrical fulleropyrrolidines were selected for reinvestigation. Through detailed spectral characterization of each isolated individual isomer, we conclude that the previously assigned structures should be corrected. In addition, the interconversion between the cis and trans isomers of the N-unsubstituted 2,5-disubstituted fulleropyrrolidines has been disclosed.

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References and notes

1. Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.
2. For reviews, see: (a) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519; (b) Tagmatarchis, N.; Prato, M. *Synlett* **2003**, 768; (c) Mateo-Alonso, A.; Sooambar, C.; Prato, M. *Org. Biomol. Chem.* **2006**, *4*, 1629.

3. (a) Shu, L.-H.; Wang, G.-W.; Wu, S.-H. *Tetrahedron Lett.* **1995**, *36*, 3871; (b) Wu, S.-H.; Sun, W.-Q.; Zhang, D.-W.; Shu, L.-H.; Wu, H.-M.; Xu, J.-F.; Lao, X.-F. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1733.
4. (a) Wilson, S. R.; Wang, Y.; Cao, J.; Tan, X. *Tetrahedron Lett.* **1996**, *37*, 775; (b) Tan, X.; Schuster, D. Y.; Wilson, S. R. *Tetrahedron Lett.* **1998**, *39*, 4187.
5. Wang, S.; Zhang, J.-m.; Song, L.-p.; Jiang, H.; Zhu, S.-z. *J. Fluorine Chem.* **2005**, *126*, 349.
6. (a) Okada, E.; Komazawa, Y.; Kurihara, M.; Inoue, H.; Miyata, N.; Okuda, H.; Tsuchiya, T.; Yamakoshi, Y. *Tetrahedron Lett.* **2004**, *45*, 527; (b) Zhang, S.; Gan, L.; Huang, C.; Lu, M.; Pan, J.; He, X. *J. Org. Chem.* **2002**, *67*, 883.
7. Banks, M. R.; Cadogan, J. I. G.; Gosney, I.; Hodgson, P. K. G.; Smith, P. R. R.; Millar, J. R. A.; Parkinson, J. A.; Rankin, D. W. H.; Taylor, A. T. *J. Chem. Soc., Chem. Commun.* **1995**, 887.
8. (a) Schick, G.; Grösser, T.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2289; (b) Smith, A. B.; Tokuyama, H. *Tetrahedron* **1996**, *52*, 5257.
9. Ovcharenko, A. A.; Chertkov, V. A.; Karchava, A. V.; Yurovskaya, M. A. *Tetrahedron Lett.* **1997**, *38*, 6933.
10. Wang, G.-W.; Yang, H.-T. *Tetrahedron Lett.* **2007**, *48*, 4635.
11. Komori, A.; Kubota, M.; Ishida, T.; Niwa, H.; Nogami, T. *Tetrahedron Lett.* **1996**, *37*, 4031.
12. The isomeric ratio should be deviated far away from 1:1 for the structure assignment by the combination of HPLC resolution and CD spectra, and compared with the assignment by ^{1}H NMR spectra.
13. In Ref. 4a, it was reported that the isomers of **1c** could not be cleanly separated by flash chromatography.
14. *cis*-**1a**: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 5.80 (s, 1H), 4.96 (q, J = 6.3 Hz, 1H), 2.13 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent) (all 1C unless indicated) δ 153.19, 152.86, 152.73, 152.66, 145.81 (2C), 145.72, 145.53, 145.26, 145.03 (2C), 144.89 (3C), 144.75 (2C), 144.57 (2C), 144.45, 144.20 (2C), 144.09 (2C), 143.98 (2C), 143.84 (3C), 143.36 (2C), 143.06 (2C), 141.89, 141.73, 141.34 (5C), 141.15, 140.92 (3C), 140.76 (4C), 140.60, 140.41, 140.25, 138.97, 138.63, 138.45, 138.16, 136.88 (aryl C), 136.18, 135.53, 134.66, 134.62, 127.47 (2C, aryl C), 127.38 (2C, aryl C), 127.10 (aryl C), 77.50 (sp^3-C of C_{60}), 75.60 (sp^3-C of C_{60}), 75.04, 66.19, 17.12; FT-IR ν/cm^{-1} (KBr) 3279, 2921, 1538, 1509, 1453, 1424, 1380, 1183, 1028, 859, 762, 748, 697, 573, 526; UV–vis ($CHCl_3$): λ_{max}/nm = 430, 307, 257. MS (-ESI) m/z 852 (M^-−1). *trans*-**1a**: ^{1}H NMR (400 MHz, CS_2/$CDCl_3$) δ 7.74 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 6.10 (s, 1H), 5.35 (q, J = 6.9 Hz, 1H), 2.20 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, CS_2/acetone-d_6 with Cr(acac)$_3$ as relaxation reagent) (all 1C unless indicated) δ 157.71, 155.53, 154.01, 153.80, 147.47, 147.45, 147.06, 146.98, 146.72, 146.58 (2C), 146.53 (2C), 146.41, 146.34, 146.25 (2C), 146.08, 145.84, 145.83, 145.77, 145.69, 145.65, 145.63, 145.60, 145.52 (2C), 145.49, 145.00, 144.82 (2C), 144.71, 143.54, 143.47, 143.04, 142.98, 142.95, 142.94, 142.86, 142.79, 142.75, 142.65, 142.63, 142.52, 142.47, 142.43, 142.40, 142.19, 142.03, 141.90, 140.50, 140.38, 140.28, 139.84, 138.82 (aryl C), 137.24, 136.88, 136.36, 135.64, 129.09 (2C, aryl C), 128.72 (2C, aryl C), 128.67 (aryl C), 79.01 (sp^3-C of C_{60}), 77.49 (sp^3-C of C_{60}), 74.04, 66.71, 22.37; FT-IR ν/cm^{-1} (KBr) 3325, 2921, 1511, 1448, 1427, 1377, 1184, 1083, 747, 697, 574, 527; UV–vis ($CHCl_3$): λ_{max}/nm = 431, 307, 259. MS (-ESI) m/z 852 (M^-−1). *cis*-**1b**: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 4.80 (q, J = 6.6 Hz, 2H), 2.02 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 153.85, 152.74, 146.62, 146.02, 145.90 (4C), 145.76, 145.62, 145.52, 145.19 (1C), 144.95 (7C), 144.76, 144.13, 143.89, 142.85 (1C), 142.61 (1C), 142.33 (4C), 142.26, 141.85, 141.79, 141.66, 141.56, 141.36, 139.86, 139.54, 136.14, 135.28, 79.27 (sp^3-C of C_{60}), 68.25, 17.51; FT-IR ν/cm^{-1} (KBr) 3272, 2960, 2921, 1426, 1376, 1184, 1086, 1032, 806, 778, 574, 554, 527; UV–vis ($CHCl_3$): λ_{max}/nm = 430, 306, 259. MS (-ESI) m/z 791 (M^-). *trans*-**1b**: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 5.07 (q, J = 6.6 Hz, 2H), 2.05 (d, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 155.73, 152.70, 146.64, 145.95, 145.84, 145.82, 145.60, 145.58, 145.41, 145.09, 144.95, 144.92, 144.88, 144.84, 144.10, 143.96, 142.82, 142.29 (4C), 142.16 (4C), 141.76 (4C), 141.49, 141.43, 139.89, 139.62, 136.12, 134.84, 78.82 (sp^3-C of C_{60}), 66.73, 20.02; FT-IR ν/cm^{-1} (KBr) 3292, 2962, 2923, 1512, 1428, 1381, 1185, 1150, 1096, 1051, 794, 779, 575, 555, 529; UV–vis ($CHCl_3$): λ_{max}/nm = 430, 308, 257. MS (-ESI) m/z 791 (M^-). *cis*-**1c**: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 7.36 (d, J = 7.2 Hz, 4H), 7.27 (t, J = 7.2 Hz, 4H), 7.17 (t, J = 7.2 Hz, 2H) 4.71 (dd, J = 10.8, 3.0 Hz, 2H), 3.84 (dd, J = 13.2, 3.0 Hz, 2H) 3.32 (dd, J = 13.2, 10.8 Hz, 2H), 2.49 (br s, 1H); ^{13}C NMR (75 MHz, CS_2/$CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 152.83, 151.96, 146.06, 145.49, 145.37, 145.25, 145.07, 144.96, 144.86, 144.64 (1C), 144.39 (1C), 144.32 (4C), 144.21, 144.08, 143.56, 143.24, 142.14 (1C), 141.95 (1C), 141.58 (4C), 141.28, 141.10, 141.00 (4C), 140.86, 140.62, 139.05, 138.69, 137.71 (aryl C), 136.21, 134.86, 128.08 (4C, aryl C), 127.94 (4C, aryl C), 125.99 (aryl C), 75.18 (sp^3-C of C_{60}), 71.15, 39.02; FT-IR ν/cm^{-1} (KBr) 3321, 3028, 2908, 2836, 1512, 1494, 1453, 1427, 1387, 1348, 1181, 1075, 891, 743, 700, 618, 574, 562, 527; UV–vis ($CHCl_3$): λ_{max}/nm = 431, 307, 257. MS (-ESI) m/z 943 (M^-). *trans*-**1c**: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 7.49–6.91 (m, 10H), 5.07 (dd, J = 10.8, 3.3 Hz, 2H), 3.64 (dd, J = 13.5, 3.3 Hz, 2H), 3.47 (dd, J = 13.5, 10.8 Hz, 2H), 2.63 (br s, 1H); ^{13}C NMR (75 MHz, CS_2/acetone-d_6 with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 156.13, 153.47, 147.47, 146.92, 146.58 (4C), 146.49, 146.33 (4C), 145.94, 145.72 (4C), 145.63, 145.53, 144.91, 144.75, 143.51, 143.00 (4C), 142.70 (4C), 142.48 (4C), 142.17 (4C), 140.58, 140.24, 139.31 (aryl C), 137.46, 136.21, 129.63 (4C, aryl C), 129.20 (4C, aryl C), 127.18 (aryl C), 76.88 (sp^3-C of C_{60}), 70.87, 40.74; FT-IR ν/cm^{-1} (KBr) 3024, 2917, 1494, 1452, 1427, 1392, 1183, 1075, 1029, 743, 721, 699, 575, 563, 552, 527; UV–vis ($CHCl_3$): λ_{max}/nm = 432, 309, 257. MS (-ESI) m/z 943 (M^-). *cis*-**1d**: ^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ 7.95 (d, J = 7.2 Hz, 4H), 7.40 (t, J = 7.2 Hz, 4H), 7.31 (t, J = 7.2 Hz, 2H), 5.96 (s, 2H); ^{13}C NMR (75 MHz, CS_2/DMSO-d_6 with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 152.71, 152.44, 145.91, 145.70, 144.96, 144.93 (4C), 144.80, 144.55, 144.46 (1C), 144.27 (1C), 144.23, 143.96, 143.90, 143.84, 143.37, 143.09, 141.85 (1C), 141.71 (1C), 141.36, 141.29, 141.06, 140.92, 140.76 (4C), 140.67, 140.23, 138.69, 138.09, 137.24 (aryl C), 135.76, 134.78, 127.54 (8C, aryl C), 127.28 (aryl C), 75.27 (sp^3-C of C_{60}), 73.93; FT-IR ν/cm^{-1} (KBr) 3316, 3028, 2922, 1511, 1454, 1427, 1377, 1277, 1184, 1027, 761, 698, 573, 547, 527; UV–vis ($CHCl_3$): λ_{max}/nm = 430, 309, 257. MS (-ESI) m/z 915 (M^-).
15. Troshin, P. A.; Peregudov, A. S.; Mühlbacher, D.; Lyubovskaya, R. N. *Eur. J. Org. Chem.* **2005**, 3064.
16. The yields of the reassigned isomers in Ref. 4a are used for the discussion.