Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

to the article

Polarizability of C_{60} fullerene dimer and oligomers: The unexpected enhancement and its use for rational design of fullerene-based nanostructures with adjustable properties

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General description

Section A. Accuracy of PBE/3ζ method applied to C_{60}, C_{70} and $(C_{60})_2$.

Section B. Mean polarizability and its exaltation for $(C_{20})_n$ (n = 1–4) calculated by PBE/3ζ and RI-PBE0/Λ1 methods.

Section C. Diagonalized tensors of polarizability calculated by PBE/3ζ method.

Section D. SI to the article includes also the optimized geometries of all the compounds studied in the work, several output files with Hessians (C_{60}, $(C_{60})_2$, $C_{60}C_{60}F_{16}$, $[C_{60}(CH_2)_5]_2$, trans 3-$(C_{60})_3$, trans 2-$(C_{60})_3$, cyclic $(C_{60})_3$). Note, Hessian calculations output files also contain non-diagonalized tensors of polarizability. All polarizability values are in a.u. (1 a.u. = 0.148 Å^3).

Output files can be open by ChemCraft or QCC Front-End programs.

Section A. Accuracy of PBE/3ζ method applied to C_{60}, C_{70} and $(C_{60})_2$

1. The comparison between the calculated and experimental parameters for C_{60} and C_{70}

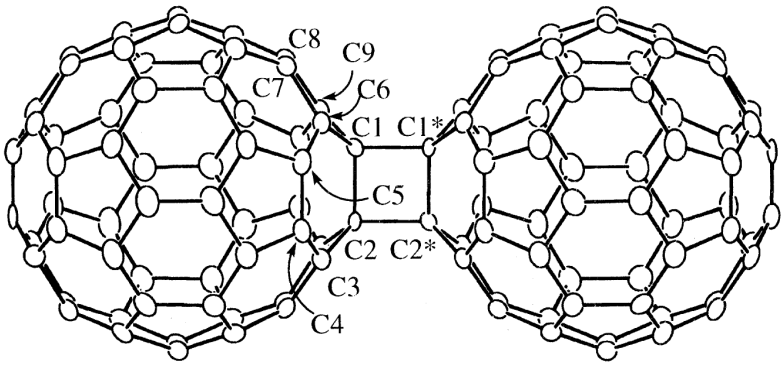
Parameters	C_{60}		C_{70}	
	PBE/3z	Experimental data	PBE/3z	Experimental data
Bond lengths (Å) [†]	5.6 bonds		***aa*** bond	
	1.453	1.458	1.452	1.453–1.463
	6.6 bonds		***ab*** bond	
	1.399	1.401	1.400	1.381–1.388
			bc bond	
			1.449	1.449–1.453
			cc bond	
			1.394	1.376–1.441
			cd bond	
			1.446	1.432–1.468
			dd bond	
			1.439	1.425–1.438
			de bond	
			1.422	1.405–1.423
			ee bond	
			1.469	1.462–1.538
IR spectra (cm^{-1}) [‡]	526 576 1179 1432	527 576 1183 1429	457 529 565 574 642 674 793 1131 1414 1430 1460	457 533 563 572 643 670 745 1130 1406 1430 1463
Entropy $S_f°$ ($J\ K^{-1}\ mol^{-1}$) [§]	549.1	544.0 (gas)	636.0	614.0 (gas)

[†] Experimentally determined bond lengths: for C_{60} – V. I. Sokolov, I. V. Stankevich, Russ. Chem. Rev. 62 (1993), 419; for C_{70} – V. V. Zverev, V. I. Kovalenko, Russ. J. Phys. Chem. A 80 (2001) 99.

[‡] IR spectra of C_{60} and C_{70} are from V. I. Sokolov, I. V. Stankevich, Russ. Chem. Rev. 62 (1993), 419.

[§] Experimental entropies for gas phase have been taken from Standard thermodynamic properties of chemical substances, CRC PRESS LLC, 2000.

2 Comparison between the calculated and experimental parameters for $(C_{60})_2$



Structural data of $(C_{60})_2$

Parameter	X-ray	PBE/3ζ
L(C1-C1*)	1,575(7)	1,598
L(C1-C2)	1,581(7)	1,599
L(C2-C3)	1,530(8)	1,522
L(C3-C4)	1,374(7)	1,383
L(C4-C5)	1,468(8)	1,48
L(C5-C6)	1,358(9)	1,383
L(C6-C1)	1,528(7)	1,522
L(C6-C7)	1,445(8)	1,438
L(C7-C8)	1,457(9)	1,452
C2-C1-C6	115,4(5)	115,24
C2-C1-C9	115,2(4)	115,24
C6-C1-C9	100,7(4)	101,189
C2-C1-C1*	90,3(4)	89,997
C1-C2-C2*	89,7(4)	90,002

X-ray structure is taken from Ref. 2

IR spectrum (cm^{-1})

Experiment	PBE/3ζ
1464	1467
1425	1433
1188	1187
770	802
762	778
746	716
710	710
612	609
574	574
560	564
551	551
548	544
527	526
480	476
449	446
419	440

Measured IR spectrum is taken from Ref. 1.

Section B. Mean polarizability and its exaltation for $(C_{20})_n$ (n = 1–4) calculated by PBE/3ζ and RI-PBE0/Λ1 methods

Molecule	PBE/3ζ		RI-PBE0/Λ1	
	α	$\Delta\alpha^{(I)}$ *	α	$\Delta\alpha^{(I)}$ *
C_{20}	27.78	–	22.45	–
$(C_{20})_2$	58.59	3.03	47.90	3.00
$(C_{20})_3$	92.88	9.54	78.25	10.90
$(C_{20})_4$	129.13	18.01	105.77	15.97

* The exaltation was calculated analogously to Equations 4 and 6:

$$\alpha_{add}^{(I)}\left((C_{20})_n\right) = n\alpha_{C_{20}}$$

$$\Delta\alpha^{(I)} = \alpha_{DFT} - \alpha_{add}^{(I)}$$

Section C. Diagonalized tensors of polarizability calculated by PBE/3ζ method

$(C_{60})_n$ and related molecules

Molecule	α_{xx}, Å^3	α_{yy}, Å^3	α_{zz}, Å^3	α, Å^3
C_{60}	82.7	82.7	82.7	82.7
$(C_{60})_2$	150.2	151.3	238.4	180.0
e-$(C_{60})_3$	326.7	287.4	215.1	276.4
trans 2-$(C_{60})_3$	218.1	231.5	405.5	285.1
trans 3-$(C_{60})_3$	216.4	253.9	376.2	282.1
trans 4-$(C_{60})_3$	355.9	265.7	217.0	279.6
Cyclic $(C_{60})_3$	206.8	317.5	318.8	281.1
Linear $(C_{60})_4$	624.0	285.6	282.6	397.4
Cyclic $(C_{60})_4$	431.3	429.6	268.5	376.4
T-shaped $(C_{60})_4$	499.7	372.8	278.4	383.6
Linear $(C_{60})_5$	831.1	352.5	348.5	510.7
"+"-shaped $(C_{60})_5$	551.3	550.4	338.6	480.1
$C_{60}C_{60}F_{16}$	150.1	158.3	240.4	183.0
$[C_{60}(CH_2)_5]_2$	172.9	172.9	252.6	199.5

C_{60} and its derivatives used for calculations in terms of additive scheme (I)

Molecule	α_{xx}, Å^3	α_{yy}, Å^3	α_{zz}, Å^3	α, Å^3
C_{60}	82.7	82.7	82.7	82.7
$C_{60}F_{16}$	71.9	95.2	95.2	87.4
$C_{60}(CH_2)_5$	88.7	95.5	95.7	93.3

Bowl-shaped hydrocarbons

Molecule	α_{xx}, Å^3	α_{yy}, Å^3	α_{zz}, Å^3	α, Å^3
$C_{21}H_{12}$	19.7	44.1	44.1	36.0
$C_{30}H_{12}$	31.5	69.0	69.4	56.6
$C_{36}H_{12}$	42.3	72.6	72.7	62.5
$C_{42}H_{18}$	110.0	110.1	49.70	90.0
$C_{50}H_{10}$	74.4	81.3	81.4	79.0

Dimers of bowl-shaped hydrocarbons

Molecule	α_{xx}, Å^3	α_{yy}, Å^3	α_{zz}, Å^3	α, Å^3
$(C_{21}H_{12})_2$	63.1	67.4	75.8	68.8
$(C_{30}H_{12})_2$	81.9	123.5	135.0	113.3
$(C_{36}H_{12})_2$	103.7	130.3	151.6	128.5
$(C_{42}H_{18})_2$	136.1	202.4	209.0	182.5
$(C_{50}H_{10})_2$	144.7	147.3	218.1	170.0

[2+2] hydrocarbon—fullerene cycloadducts

Molecule	α_{xx}, Å^3	α_{yy}, Å^3	α_{zz}, Å^3	α, Å^3
$C_{60}C_{21}H_{12}$	107.3	113.9	145.0	122.1
$C_{60}C_{30}H_{12}$	126.8	137.4	172.9	145.7
$C_{60}C_{36}H_{12}$	133.3	140.8	187.3	153.8
$C_{60}C_{42}H_{18}$	159.3	177.5	209.0	182.0
$C_{60}C_{50}H_{10}$	148.1	148.7	228.4	175.1