EXPERIMENTAL AND COMPUTED DIPOLE MOMENTS IN DONOR–BRIDGE–ACCEPTOR SYSTEMS WITH *p*-PHENYLENE AND *p*-CARBORANEDIYL BRIDGES

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Dedicated to the memory of Professor Otto Exner.

Dipole moments were measured for a series of substituted benzenes, biphenyls, terphenyls, *C*-monoaryl- and *C,C'*-diaryl-*p*-carboranes. For the donor–bridge–acceptor systems, $Me_2N–X–NO_2$, where X is 1,4-phenylene, biphenyl-4,4′-diyl, terphenyl and $1,4-C_6H_4-p-CB_{10}H_{10}C-1,4-C_6H_4$, the measured interaction dipole moments are 1.36, 0.74, 0.51 and 0.00 D, respectively. The magnitude of the dipole moment reflects the ability of the bridge to transmit electronic effects between donor and acceptor groups. Thus, whilst the 1,4-phenylene bridges allow moderate electronic interactions between the remote groups, the *p*-carboranediyl unit is less efficient as a conduit for electronic effects. Averaged dipole moments computed at the DFT (B3LYP/6-31G*) level of theory from two distinct molecular conformers are in good agreement with the experimental values. Examination of the calculated electronic structures provides insight into the nature of the interactions between the donor and acceptor moieties through these 2D and 3D aromatic bridges. The most significant cooperative effect of the bridge on the dipole moment occurs in systems where there is some overlap between the HOMO and LUMO orbitals. This orbital overlap criterion may help to define the difference between "push-pull" systems in which electronic effects are mediated by the bridging moiety, and simpler systems in which the bridge acts as an electronically innocent spacer unit and through-space charge transfer/separation is dominant.

Keywords: Donor–Bridge–Acceptor systems; Terphenyls; *p*-Carboranylenes; Dipole moments; HOMO-LUMO; Electronic transmission; Carboranes; Substituent effects, DFT calculations.

Current interest in donor–bridge–acceptor systems in which the donor and acceptor moieties are linked by a bridge mediating interaction between them stems from the large excited-state dipole moments that can arise by photoinduced intramolecular charge transfer. Large differences between the ground and excited state dipole moments can lead to a significant non-linear optical response[1]. Weakly coupled donor–bridge–acceptor systems are also of interest as potential candidates for molecular scale rectifiers[2]. We are currently interested in surveying various bridging elements for their ability to act as efficient conduits of electronic effects in donor–bridge–acceptor systems; here we report dipole moment measurements on systems where the bridge consists of one, two or three 1,4-phenylene units, **1**–**3** (Chart 1). Similar data from a related system containing a *p*-carboranediyl unit, -CB$_{10}$H$_{10}$C-, **4**, permits a comparison of the relative efficacy of the *p*-carboranediyl and 1,4-phenylene moieties as conduits for electronic effects between 4-(dimethylamino)phenyl and 4-nitrophenyl moieties.

1 6.93 D

3 6.75 D

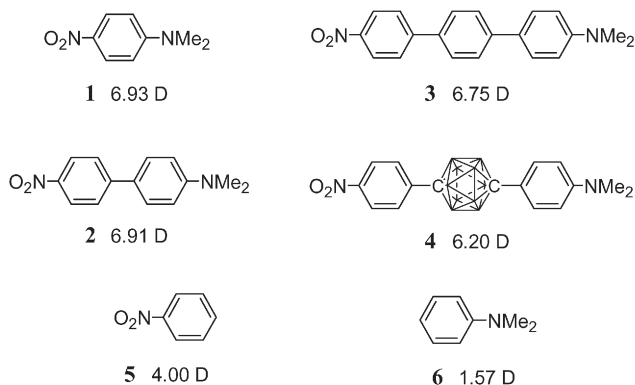**2** 6.91 D

4 6.20 D

5 4.00 D

6 1.57 D

CHART 1

Dipole moment measurements have been used to estimate the electron distribution, and hence interactions between donor and acceptor groups, in molecules since the early 1930s. In the case of a typical linear donor–bridge–acceptor compound D–X–A, assuming the constituent dipole moments to be colinear, the difference between the vector sum of the dipole moments of monofunctional model systems, H–X–A (μ_A) and D–X–H (μ_D), and that of the bifunctional compound D–X–A (μ_{DA}) represents an interaction (or mesomeric) moment μ_{int} (ref.[3]).

$$\mu_{int} = \mu_{DA} - (\mu_D + \mu_A) \tag{1}$$

From values of μ_{DA} 6.93 D for **1**, μ_A 4.00 D for nitrobenzene (**5**) and μ_D 1.57 D for *N,N*-dimethylaniline (**6**) (Chart 1), Eq. (*1*) gives μ_{int} = 1.36 D for the simple 1,4-phenylene compound **1**. This large μ_{int} value, which is one of the highest interaction moments measured, is indicative of the ability of the 1,4-phenylene bridge to permit interactions between the remote groups[4]. Here we report the dipole moments of 4-(dimethylamino)-4″-nitrobiphenyl (**2**) and 4-(dimethylamino)-4″-nitro-*p*-terphenyl (**3**) and discuss the effect of inserting additional 1,4-phenylene units into the bridging moiety on the interaction moment in comparison with that of **1**. Since the *p*-C⋯C distances in benzene and *closo*-1,12-$C_2B_{10}H_{12}$, *p*-carborane, are similar (2.77 and 3.04 Å, respectively[5]), we have also measured dipole moments of selected aryl-*p*-carboranes. This is, to the best of our knowledge, the first report of experimentally determined dipole moments of aryl-*p*-carboranes. In addition, the donor–acceptor-substituted carborane system 1-[4-(dimethylamino)phenyl-12-(4-nitrophenyl)-*p*-carborane[6] (**4**) has been compared with 4-(dimethylamino)-4″-nitro-*p*-terphenyl (**3**) to assess the relative ability of the cage and 1,4-phenylene to act as a transmitter of electronic interactions, as determined by dipole moment measurements. The ability of the *p*-carboranediyl unit as a transmitter of electronic interactions has been investigated by other techniques and the general consensus so far has been that the cage can transmit electron density[7].

The experimental dipole moments measured for aromatic and carborane compounds with the widely used NMe₂ donor and NO₂ acceptor groups were compared with computed dipole moments. The dipole moments calculated for a weighted average of the rotational conformers are in good agreement with the experimental data. The experimental interaction (or mesomeric) moments μ_{int} are also reproduced well by computations.

EXPERIMENTAL

Syntheses

The biphenyls and arylcarboranes used in this work and listed in Table I were purchased from commerical sources and used as received, or prepared according to the literature procedures[6,8]. Compound **3** was prepared from *p*-terphenyl as detailed below. ^{1}H and ^{13}C NMR spectra (δ, ppm; *J*, Hz) were measured on a Varian Inova 400 instrument with TMS as an internal standard, IR spectra (ν_{max}, cm^{-1}) were measured on a Perkin–Elmer 684 FTIR instrument.

Synthesis of 4-(Dimethylamino)-4″-nitro-*p*-terphenyl (**3**)

a) 4,4″-Dinitro-p-terphenyl[9]. A sample of *p*-terphenyl (2.76 g, 12 mmol) was dissolved in a hot mixture of acetic acid (100 ml, 98%) and acetic anhydride (2 ml). Fuming HNO_3 (15 ml)

was added dropwise to the stirred solution over 2 h. The resulting mixture was cooled, the precipitated 4,4″-dinitro-*p*-terphenyl collected by filtration and washed with water. Recrystallization from pyridine gave yellow needles. Yield 0.95 g (25%), m.p. 273–274 °C (ref.[9] gives 272–274.5 °C). ^{1}H NMR (pyridine-d_5, 60 °C): 7.86 (4 H, s); 7.87 (4 H, m); 8.35 (4 H, m). ^{13}C NMR (pyridine-d_5, 60 °C): 124.5, 128.19, 128.55, 139.38, 146.65, 147.91.

TABLE I
Measured ground-state dipole moments and measured interaction moments (where available) in debye (D) for donor–bridge–acceptor (D–X–A) and monofunctional (H–X–A and D–X–H) systems in benzene

Compd	D/H	X	A/H	$\mu_{exp}{}^a$	$(\mu_D + \mu_A)^b$	$\mu_{int}{}^c$
1	Me_2N	C_6H_4	NO_2	6.93	5.57	1.36
2	Me_2N	$C_6H_4-C_6H_4$	NO_2	6.91	6.17	0.74
3	Me_2N	$C_6H_4-C_6H_4-C_6H_4$	NO_2	6.75	6.24	0.51
4	Me_2N	$C_6H_4-CB_{10}H_{10}C-C_6H_4$	NO_2	6.20	6.20^d	0.00
5	H	C_6H_4	NO_2	4.00		
	H_2N	C_6H_4	H	1.56^e		
6	Me_2N	C_6H_4	H	1.57^e		
	H_2N	C_6H_4	NO_2	6.27	5.56	0.71
9	H	$C_6H_4-C_6H_4$	NO_2	4.32		
10	Me_2N	$C_6H_4-C_6H_4$	H	1.85		
	H_2N	$C_6H_4-C_6H_4$	NO_2	6.42	6.17	0.25
	H	$C_6H_4-C_6H_4-C_6H_4$	NO_2	4.40		
	Me_2N	$C_6H_4-C_6H_4-C_6H_4$	H	1.84		
	H_2N	$C_6H_4-C_6H_4-C_6H_4$	NO_2	6.18		
7	H	$C_6H_4-CB_{10}H_{10}C$	NO_2	3.88		
	H	$C_6H_4-CB_{10}H_{10}C$	CF_3	2.36		
8	Me_2N	$C_6H_4-CB_{10}H_{10}C$	H	2.32		
	MeO	$C_6H_4-CB_{10}H_{10}C$	H	1.62		
	HO	$C_6H_4-CB_{10}H_{10}C$	H	1.73		
	MeO	$C_6H_4-CB_{10}H_{10}C-C_6H_4$	NO_2	4.85		
	HO	$C_6H_4-CB_{10}H_{10}C-C_6H_4$	NO_2	4.77		

^{a} μ_{exp}, measured dipole moment. ^{b} From μ_{exp} values of monofunctional systems D–X–H and H–X–A defined as μ_D and μ_A, respectively. ^{c} μ_{int}, values based on Eq. (*1*). ^{d} From μ_{int} values of **7** and **8** for μ_A and μ_D, respectively. ^{e} Taken from ref.[19]

b) 4-Amino-4''-nitro-p-terphenyl[10]. A solution of 4,4''-dinitro-*p*-terphenyl (0.45 g, 1.40 mmol) in pyridine (11.5 ml) was refluxed for 1 h before a solution of $Na_2S \cdot 9H_2O$ (0.5 g, 2.11 mmol) in water (22 ml) saturated with H_2S was added over 1 h. After 30 min, the mixture was cooled and an orange precipitate was separated by filtration. The crude product was dissolved in DMF (5 ml), silica gel (2 g) was added and the solvent was removed in vacuo. Flash chromatography on silica (benzene–dichloromethane–DMF 60:30:1) gave an orange powder identified as 4-amino-4''-nitro-*p*-terphenyl. Yield 186 mg (46%), m.p. 302–303 °C (ref.[10] gives 300–301 °C). IR (Fluorolube®): 3489 (N–H), 3388 (N–H), 1499 (NO_2), 1337 (NO_2). ^1H NMR (DMSO-d_6): 5.33 (2 H, s); 6.66 (2 H, m); 7.46 (2 H, m); 7.7 (2 H, m); 7.79 (2 H, m); 7.99 (2 H, m); 8.30 (2 H, m). ^{13}C NMR (DMSO-d_6): 114.2, 124.1, 125.8, 126.0, 127.2, 127.3, 127.6, 134.6, 141.3, 146.29, 146.32, 148.9.

c) 4-(Dimethylamino)-4''-nitro-p-terphenyl (**3**)[11]. A mixture of 4-amino-4''-nitro-*p*-terphenyl (150 mg, 0.516 mmol) and dimethyl sulfate (0.4 ml, 4.2 mmol) was heated until all the solid dissolved. Powdered K_2CO_3 (600 mg, 4.26 mmol) and DMF (2 ml) were added. This paste was heated in a microwave oven (800 W output) for 5 s, stirred and again heated for 12 s. The cooled mixture was extracted with warm DMF (4 × 4 ml), the extract was concentrated to 6 ml using a rotary evaporator and silica gel (4 g) was added. The resulting paste was dried in vacuo (0.01 mm Hg at 100 °C). Flash chromatography on silica (benzene–ethyl acetate 2:1) gave 4-(dimethylamino)-4''-nitro-*p*-terphenyl as an orange powder. Yield 52 mg (46%), m.p. 320–321 °C (ref.[11] gives 319–320 °C). ^1H NMR (DMSO-d_6): 2.96 (6 H, s); 6.17 (2 H, d, m); 7.44 (2 H, m); 7.80 (2 H, m); 7.81 (2 H, m); 7.98 (2 H, m); 8.30 (2 H, m). ^{13}C NMR (DMSO-d_6): 41.4, 107.2, 122.1, 125.2, 126.0, 127.2, 127.3, 127.6, 134.6, 141.3, 146.29, 146.32, 148.9.

Dipole Moments

Dipole moments were determined at 25 °C in benzene (usually with five solutions, weight fractions (%) from 2.0×10^{-4} to 1.2×10^{-3}; for substituted *p*-terphenyls, due to their very limited solubility in benzene, concentrations were in the range from 3.2×10^{-5} to 1.1×10^{-4} mol l^{-1}); relative permittivities were measured at 6 MHz in home-made equipment[12] with direct frequency reading. Refractive indices were measured on an Aerograph Refractive Index Detector (Varian). The dipole moments were obtained by extrapolation to infinite dilution by the methods of Guggenheim[12] and Smith[13].

Computational Details

All computations were carried out with the Gaussian03 package[14]. Geometry optimizations were carried out at the B3LYP/6-31G* level of theory[15,16], without symmetry constraints. Frequency computations with the optimized geometries gave no imaginary frequencies, indicating the geometries are true minima. The use of the HF/6-31G* and MP2/6-31G* levels gave similar geometries except for the dimethylamino group that can be pyramidal or planar. The computed dipole moments at these three levels of theory are similar and, thus, only results obtained at the B3LYP/6-31G* level of theory are discussed here. Geometries with constrained torsion angles were also optimized and found from frequency calculations to have imaginary frequencies (usually one for every torsion angle constrained). There is a good agreement between the geometrical parameters for geometries computed here and experimental X-ray data of related compounds[17,18], which gives a further degree of confidence in the accuracy of the calculations.

RESULTS AND DISCUSSION

Dipole Moment Measurements

Dipole moments (μ_{exp}) were measured for a series of aromatic compounds in benzene (Table I). The "push-pull" terphenyl **3** was synthesized in three steps from *p*-terphenyl as detailed in Experimental.

The interaction (or mesomeric) moments μ_{int} 1.36, 0.74 and 0.51 D for **1**, **2** and **3**, respectively, can be calculated from Eq. (*1*), using the measured dipole moments of the related monosubstituted derivatives, D–X–H and H–X–A (Table I). The interaction moments decrease with the increasing number of 1,4-phenylene units and, hence, the increasing donor–acceptor N···N distance (N···N (in Å): 5.4 (**1**), 9.9 (**2**) and 14.3 (**3**)). Nevertheless, the variation of μ_{int} is nonlinear with distance, and the interaction moment for **3** remains substantial, indicating that the *p*-terphenyl-4,4″-diyl bridge can transmit long-range electronic interactions.

The dipole moments of the monoaryl-*p*-carboranes containing NO_2 (1-(4-nitrophenyl)-*p*-carborane (**7**)) and NMe_2 (1-[4-(dimethylamino)phenyl-*p*-carborane (**8**)) groups in the *para* positions of the benzene ring (Chart 2) are 3.88 and 2.32 D, respectively. A comparison of these data with the dipole moments of 4.32 and 1.85 D in biphenyls, 4-nitrobiphenyl (**9**) and 4-(dimethylamino)biphenyl (**10**) (Chart 2) shows that the *p*-carborane-1,12-diyl is a stronger electron acceptor than the phenyl group, manifested by the change in dipole moment by ±0.4 D. The *o*-carborane analogue of **7**, where the cage carbons occupy adjacent vertices, has a dipole moment of 4.50 D [20] and, thus, is an even stronger acceptor than the *p*-carborane cage.

O_2N—〈 〉—C〈carborane〉CH
7 3.88 D

HC〈carborane〉C—〈 〉—NMe_2
8 2.32 D

O_2N—〈 〉—〈 〉
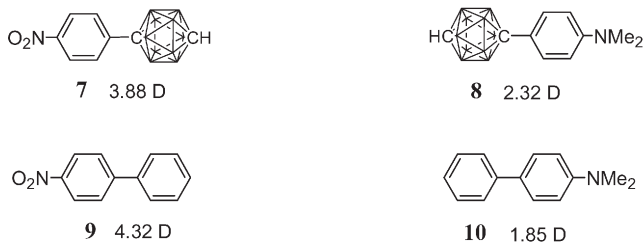**9** 4.32 D

〈 〉—〈 〉—NMe_2
10 1.85 D

CHART 2

The measured dipole moment of the donor–bridge–acceptor carborane-diyl system diphenyl-*p*-carborane **4** (6.20 D) is the sum of dipole moments of the partial model systems **7** and **8**. The N···N distance is similar in both **3**

(14.3 Å) and **4** (14.6 Å), yet the dipole moment of **4** is some 0.55 D smaller than that of terphenyl **3**. Clearly, the introduction of the better electron acceptor carborane cage decreases the overall molecular dipole moment. There is little evidence for a "cooperative" effect leading to an increased dipole moment in comparison with the sum of the components.

Dipole Moment Computations

The low-energy barriers to some rotations of the rings, cages, NMe_2 and NO_2 groups around the various N–C and C–C bonds leads to a population of a range of molecular conformations in solution, and, therefore, the measured dipole moments in Table I correspond to the weighted average of rotational conformers. This non-uniform set of molecular geometries leads to fundamental difficulties when comparing experimental data with those calculated from a single static optimized geometry[21].

Rotation Effects on Calculated Dipole Moments

Full geometry optimization of nitrobenzene at the B3LYP/6-31G* level of theory gave a calculated dipole moment of 4.58 D with the coplanar nitro group in (**5A** in Chart 3). When the nitro group is constrained to be perpendicular (**5B**) to the ring, the calculated dipole moment is 4.02 D.
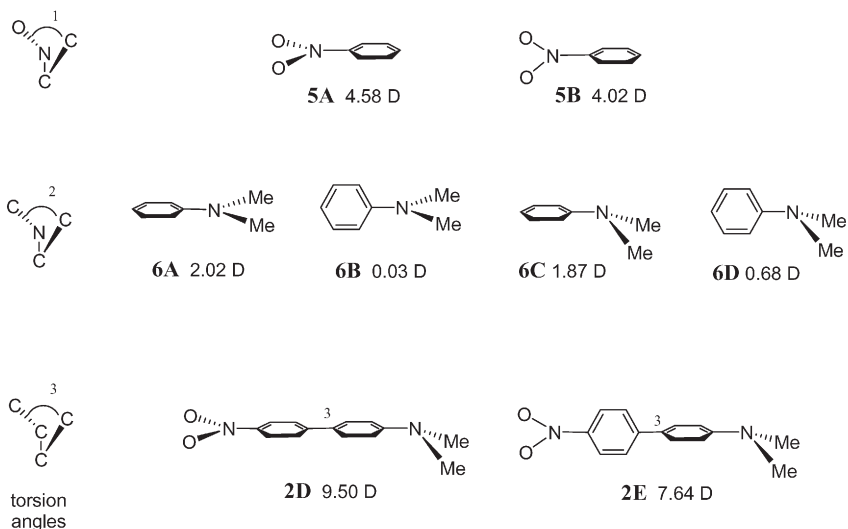

CHART 3

Clearly, the orientation of the ring and NO_2 groups and, hence, the conjugation between the two π-systems, plays a role in determining the calculated dipole moment. A model for the population distribution can be constructed by considering a set of conformationally constrained molecules in which the C–C–N–O torsion angle (ω_1) between the plane of the aromatic ring and the nitro group is varied between 0 and 90° in 10° steps. The numerical average of the resulting ten calculated dipole moments is 4.35 D.

The energy barrier between the pyramidal and planar geometries of NMe_2 is known to be small, and, consequently, the preference of one form over the other depends on the level of theory used[22]. A full geometry optimization of *N,N*-dimethylaniline gave a geometry (**6C**, **C** is defined here and elsewhere as a true minimum if different from the planar geometry **A** (see Chart 3)) with a pyramidal NMe_2 group at the B3LYP/6-31G* level of theory. With the degree of pyramidalization of the NMe_2 group unconstrained, the calculated dipole moment of the geometry with the C–C–N–C torsion angle (ω_2) at 0° (**6A**: a planar NMe_2 group is obtained) is 2.02 D whereas at ω_2 = 90° (**6D** where a pyramidal NMe_2 group is preferred) is 0.68 D and the numerical average of the ten model geometries derived from stepwise rotation of the torsion angle ω_2 is 1.33 D. However, when the NMe_2 group is constrained to be planar, the calculated dipole moment at ω_2 = 90° is 0.03 D (**6B**) and, therefore, the average of ten calculated dipole moments with planar NMe_2 groups is lower than 1.08 D. The very large variation in the calculated dipole moment as a function of both the geometry at nitrogen (planar/pyramidal) and the relative orientation of the NMe_2 group with respect to the plane of the aryl ring is remarkable.

The influence of rotation of two benzene rings on the dipole moment of the biphenyl compounds was also examined, using **2** as a typical example. The dipole moment was calculated for a series of models with only the inter-ring C–C–C–C torsion angle (ω_3) being constrained at 10° intervals. The computed dipole moments vary between 9.50 D (ω_3 = 0°, **2D**) and 7.64 D (ω_3 = 90°, **2E**) with a number weighted average of 8.64 D.

In the case of the monoaryl carboranes **7** and **8**, rotation of the carborane group, which has a very small unique rotation range of 18° compared with 90° for a phenyl group, has little influence on the computed dipole moments that vary by only 0.06 D for **7** and 0.10 D for **8**. Given the negligible effect of the rotation of the cage on dipole moments, the *p*-carborane cage can be considered cylindrically symmetrical in much the same fashion as an ethynyl (or diynyl) group.

Comparison of Measured and Computed Dipole Moments

The preceding studies indicate that, in regard to the calculated dipole moments, the most significant conformational changes in compounds **1**–**6** concern the angles ω_2 and ω_3. The position of the nitro group, expressed by ω_1, is less significant, but still worthy of inclusion in the overall assessment of the molecular dipole moment. However, the carboranediyl cage in **4** can be regarded as offering effectively cylindrical symmetry and, hence, rotation effects around the C_{aryl}–C_{cage} bonds can be neglected. In addition, the average dipole moment calculated from simply two values of 0 and 90° for both ω_1 and ω_2 is similar to that obtained by averaging the calculated dipole moments from ten conformational models in which ω_1 and ω_2 are stepped in 10° increments. To simplify the treatment, average dipole moments were calculated for the series in Table II from models with torsion angles constrained to $\omega_1 = \omega_2 = \omega_3 = 0°$ for μ_0 and $\omega_1 = \omega_2 = \omega_3 = 90°$ for μ_{90}. These models are labeled **A** and **B**, respectively, to represent these specific constraints for all the systems discussed here. The NMe_2 group was constrained to be planar in all cases. The dipole moments (μ_{full}) calculated from the most stable fully optimized geometries (which were found to be non-planar for those containing NMe_2 and biphenyl groups) and the experimentally determined dipole moments (μ_{exp}) are also included in Table II for the purpose of comparison. There is good general agreement between the observed and average computed dipole moments for all compounds in Table II, despite the fact that the averaged dipole moments are computed from only two conformers. A more accurate computed dipole moment on a molecule would be expected from a time-consuming and computationally-intensive analysis of all possible conformers, weighted against the conformational population distribution in solution at room temperature which might be estimated from the relative energies of the conformers. However, such estimates are extremely complex as the influence of the surrounding solvent molecules on the conformational distribution and local dipoles should also be considered.

Table III shows the computed interaction moments calculated for compounds **1**–**4**, with $\omega_1 = \omega_2 = \omega_3 = 0°$ (**A**) and $\omega_1 = \omega_2 = \omega_3 = 90°$ (**B**), together with the interaction moments (μ_{int}) calculated from experimental data where available. The computed interaction moments ($\mu_{int(0)}$) for the planar geometries agree very well with the observed interaction moments for **1**–**4**. The computed interaction moments for the perpendicular geometries ($\mu_{int(90)}$) are negative and generally small. The averaged interaction moments computed are based on two extreme conformations that are assumed

TABLE II

Comparison of measured and computed dipole moments in debye (D) for selected donor–bridge–acceptor (D–X–A) and monofunctional (H–X–A and D–X–H) systems

D/H	X	A/H	Compd	μ_{full} [a]	μ_0 [b]	μ_{90} [c]	$\dfrac{(\mu_0 + \mu_{90})}{2}$	μ_{exp} [d]	$\Delta\mu$ [e]
O_2N	C_6H_4	NMe_2	**1**	8.07	8.07	4.66	6.37	6.93	0.56
O_2N	$C_6H_4-C_6H_4$	NMe_2	**2**	9.03	9.56	4.96	7.26	6.91	−0.35
O_2N	$C_6H_4-C_6H_4-C_6H_4$	NMe_2	**3**	9.29	10.30	5.08	7.69	6.75	−0.94
O_2N	$C_6H_4-CB_{10}H_{10}C-C_6H_4$	NMe_2	**4**	8.62	8.72	5.43	7.08	6.20	−0.88
O_2N	C_6H_4	H	**5**	4.58	4.58	4.02	4.30	4.00	−0.30
H	C_6H_4	NMe_2	**6**	1.86	2.02	0.68	1.35	1.57	0.22
O_2N	$C_6H_4-C_6H_4$	H	**9**	5.51	5.69	4.47	5.08	4.32	−0.76
H	$C_6H_4-C_6H_4$	NMe_2	**10**	2.55	2.94	0.70	1.82	1.85	0.03
O_2N	$C_6H_4-C_6H_4-C_6H_4$	H		5.97	6.30	4.65	5.47	4.40	−1.07
H	$C_6H_4-C_6H_4-C_6H_4$	NMe_2		2.86	3.42	0.72	1.79	1.84	−0.05
O_2N	$C_6H_4-CB_{10}H_{10}C-C_6H_4$	H		5.54	5.54	4.76	5.15	–	
H	$C_6H_4-CB_{10}H_{10}C-C_6H_4$	NMe_2		2.89	3.00	0.63	1.82	–	
O_2N	$C_6H_4-CB_{10}H_{10}C$	H	**7**	4.46	4.46	3.70	4.08	3.88	−0.20
H	$CB_{10}H_{10}C-C_6H_4$	NMe_2	**8**	3.60	3.70	1.41	2.56	2.32	−0.24

[a] Computed dipole moment of the fully optimized geometry – true minimum. [b] Computed dipole moment of the planar geometry – torsion angles ω_1, ω_2 and $\omega_3 = 0°$. [c] Computed dipole moment of the planar geometry – torsion angles ω_1, ω_2 and $\omega_3 = 90°$. [d] Measured dipole moment. [e] Average computed value $(\mu_0 + \mu_{90})/2 - \mu_{exp}$.

to be equally populated in solution for convenience. While the averaged interaction moments computed are clearly underestimated compared to observed interaction moments, the trends of the averaged interaction moments are in agreement with the observed trends.

TABLE III
Comparison of measured and computed interaction moments in debye (D)

Compd	$\mu_{int}{}^a$	$\mu_{int(0)}{}^b$	$\mu_{int(90)}{}^c$	$(\mu_{int(0)} + \mu_{int(90)})/2^d$
1	1.36	1.47	–0.04	0.72
2	0.74	0.93	–0.21	0.36
3	0.51	0.58	–0.10	0.24
4	0.04	0.19	–0.16	0.02

[a] Measured interaction moment. [b] Computed interaction moment from μ_0 values in Table II. [c] Computed interaction moment from μ_{90} values in Table II. [d] Average computed interaction moment.

Electronic Structure Computations

Molecular orbital calculations were carried out on the three 1,4-phenylene systems **1**–**3** where the geometries are fully planar (**A**, ω_1, ω_2 and $\omega_3 = 0°$) or fully perpendicular (**B**, ω_1, ω_2 and $\omega_3 = 90°$) with the NMe_2 group constrained to be planar. In addition, Table IV shows orbital energies and percentage orbital group compositions for the geometry **1A**, containing all groups (NO_2, NMe_2, C_6H_4) in plane, and for the geometry **1B** with each group perpendicular to each other. The HOMO and LUMO for the planar (**A**) and perpendicular (**B**) geometries of **1**–**3** involve all three groups but the perpendicular geometries contain HOMOs largely localized at the amino groups and LUMOs largely localized at the nitro groups. Clearly, the orientational dependence of the π-orbitals in the 1,4-phenylene unit reflects the ability of the 1,4-phenylene unit to transmit electronic interactions between donor and acceptor groups (i.e., to mix the donor- and acceptor-localized wavefunctions).

The 1,12-carborane-1,12-diyl system **4**, in which the orientation of the cage has a small effect on the computed dipole moment, was compared with the structurally similar all-1,4-phenylene system **3**. Two geometries of *p*-terphenyl **3** were considered in which the central 1,4-phenylene unit is either simply constrained to be planar ($\omega_3 = 0°$, **3D**) or perpendicular ($\omega_3 = 0°$, **3E**) to the neighboring phenylene units. The computed dipole mo-

Orbital energies and percentage orbital compositions for planar and perpendicular geometries **1A** and **1B**, respectively

MO		eV	NO_2	C_6H_4	NMe_2
1A (0°), total energy E = –570.72352 hartree					
47	L+2	0.71	25	67	8
46	L+1	–0.38	0	99	1
45	LUMO	–1.83	65	30	5
44	HOMO	–5.82	6	50	44
43	H-1	–7.27	5	95	0
42	H-2	–7.33	97	3	0
1B (90°), total energy E = –570.70099 hartree					
47	L+2	–0.62	3	92	5
46	L+1	–0.67	0	99	1
45	LUMO	–1.89	96	4	0
44	HOMO	–6.13	3	26	72
43	H-1	–7.25	29	51	20
42	H-2	–7.46	1	98	0

ments for **3D**, **3E** and the fully optimized geometry **4C** are 10.14, 7.79 and 8.62 D, respectively. The frontier orbitals (HOMO and LUMO) for the three geometries are shown in Fig. 1. The orbital energies and group orbital contributions are listed in Table V.

It is clear from the computed data that geometries **3E** and **4C** have similar electronic structures, which is also reflected in the similar values of the calculated dipole moments. In each case, **3E** and **4C**, the HOMO and LUMO, respectively, are localized on the $NMe_2C_6H_4$- and $NO_2C_6H_4$- groups, with little involvement of the central cage or 1,4-phenylene unit. The *p*-carboranediyl plays a similar role as a 1,4-phenylene; the latter is forced to adopt a perpendicular orientation to the $NO_2C_6H_4$- and $NMe_2C_6H_4$-groups and both act as spacers or weak transmitters of electronic interactions between donor and acceptor groups. In contrast, both HOMO and LUMO for the planar geometry **3D** involve significant contributions from the central part of the bridging moiety.

TABLE V
Orbital energies and percentage orbital compositions for **3D**, **3E** and **4C**

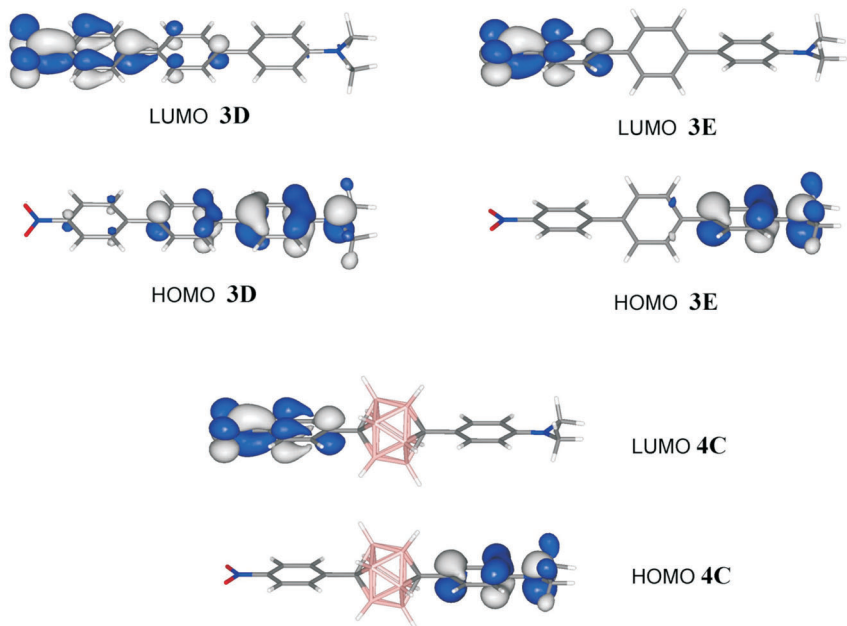| MO		eV	NO_2	$C_6H_4(NO_2)$	C_6H_4	$C_6H_4(NMe_2)$	NMe_2
p-Terphenyl **3D**, E = –1032.82992 hartree							
88	L+3	–0.21	0	27	23	50	1
87	L+2	–0.62	0	66	28	6	0
86	L+1	–1.01	24	11	40	22	3
85	LUMO	–2.32	49	35	12	3	1
84	HOMO	–5.14	1	5	19	45	31
83	H-1	–6.46	3	29	38	11	19
82	H-2	–6.86	0	1	22	78	0
81	H-3	–7.03	0	4	74	22	0
p-Terphenyl **3E**, E = –1032.82470 hartree							
88	L+3	–0.19	0	17	50	32	0
87	L+2	–0.22	0	3	94	3	0
86	L+1	–0.74	0	80	18	2	0
85	LUMO	–2.31	64	34	1	0	0
84	HOMO	–5.21	0	0	2	53	45
83	H-1	–6.68	0	0	6	93	0
82	H-2	–6.77	0	4	91	5	0
81	H-3	–6.96	0	2	92	6	0
Carborane **4C**, E = –1132.67788 hartree							
104	L+3	–0.24	0	3	10	86	1
103	L+2	–0.73	15	18	47	17	2
102	L+1	–0.89	0	90	8	1	0
101	LUMO	–2.51	59	36	4	0	0
100	HOMO	–5.43	0	0	4	51	45
99	H-1	–6.94	0	0	1	99	0
98	H-2	–7.54	5	69	12	7	7
97	H-3	–7.63	3	96	1	0	0

Fig. 1

Frontier orbitals for computed geometries of *p*-terphenyl **3D**, *p*-terphenyl **3E** and carborane **4C**

CONCLUSIONS

Dipole moments were measured for the three systems **1**–**3** where one, two or three 1,4-phenylene unit(s) are linked to donor NO_2 group and acceptor NMe_2 group. The interaction moments in benzene (**1**), biphenyl (**2**) and terphenyl (**3**) decrease as the number of 1,4-phenylene units in the bridge increases. Nevertheless, the substantial interaction moments show that the phenylene bridges are moderate conduits of electron interactions in these "push-pull" systems. By contrast, the interaction moment for the system **4** where a *p*-carborane-1,12-diyl unit replaces the central 1,4-phenylene unit in terphenyl **3**, is very small. The *p*-carboranylene unit contributes little to promoting donor–acceptor electron interactions in these "push-pull" systems and can be described as a spacer.

The dipole moments for these systems, computed at the DFT (B3LYP/6-31G*) level of theory, depend on the conformation of their molecular geometries where planar and perpendicular geometries offer the highest and lowest computed dipole moments, respectively. The agreement between measured

and average calculated dipole and interaction moments for aromatics and arylcarboranes are acceptable. Dipole moment computations at the DFT level of theory may therefore be used for prediction of the ability of the bridge to transmit electronic interactions between donor and acceptor groups when many conformers expected in solution are taken into account. Based on electronic structure computations, the orientation dependence of the π-orbitals in the 1,4-phenylene unit reflects its ability to transmit electronic interactions between donor and acceptor groups. If the central 1,4-phenylene unit in **3** is constrained to be perpendicular to its neighboring rings, the frontier orbitals for **3** remarkably resemble those for the related carborane **4**.

Therefore, it can be concluded that the most significant cooperative effect of the bridge on the dipole moment occurs in systems where there is some overlap between the HOMO and LUMO orbitals. This orbital overlap criterion may help define the difference between "push-pull" systems, in which electronic effects are mediated by the bridging moiety, and simpler systems in which the bridge acts as an electronically innocent spacer-unit and through space charge transfer/separation is dominant.

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