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The geometric structure, dipole moment, μ, linear polarizability, α and first hyperpolarizability, β, of symmetrically substituted amino- and cyanobenzofurobenzofurans and dihydrobenzofurobenzofurans have been calculated by *ab initio* coupled perturbed Hartree-Fock methods. Singlet electronic transition energies and excited state dipole moments have been calculated by the AM1 program. The benzofurobenzofuran derivatives are planar, while dihydrobenzofurobenzofuran derivatives have a V-shaped form, in agreement with experimental X-ray data. The molecular structure is rather unaffected by substitution. The linear polarizability is weakly sensitive to the substituent and substituent position, while β value changes over about 1 order of magnitude. Although both series of compounds have relatively modest hyperpolarizability, reaching *ca.* 60% β of *para*-nitroaniline, they have good properties for second harmonic generation devices: transparency in the visible spectral region, thermal stability and conformational rigidity.

Introduction.

The search on molecular systems with nonlinear optical properties useful in optoelectronic applications is actively pursued [1,2]. The theoretical prediction of nonlinear optical coefficients (in terms of (hyper)polarizability), in relation to the electronic and molecular structure, is a valid contribution in practical projecting of suitable materials. Knowledge gained indicates that in organic molecules intrinsically large hyperpolarizability is associated with charge transfer in delocalized π-electron systems. *Para*-nitroaniline is a prototype system. Many electron-donor-acceptor molecules have been investigated. Delocalized π-electron acting nonlinear repeat units may be conveniently used in polymer or poled polymer technology to have usefully processable nonlinear optical materials. Among others, needed characteristics of such materials for second harmonic generation devices are: i) optical transparency and ii) thermal and environmental stability. In this respect benzofurobenzofuran and dihydrobenzofurobenzofuran step-ladder polymers [3] are of potential use having excellent thermal and chemical stability together with transparency in the visible and near ultraviolet spectral region. Ladder polymers are of great current interest as nonlinear optical materials [4-7]. In this work we report our theoretical results of the geometric and optical properties of symmetrical substituted benzofurobenzofuran and dihydrobenzofurobenzofuran monomers (Figure 1). The reported quantities are the ground and excited-state dipole moments, μ, electronic excitation energy, ΔE, linear polarizability, α, and first hyperpolarizability, β. The substituent effect of electron donor and electron acceptor groups is represented by the classical amino and cyano groups.

Computational Methods.

Molecular geometries were optimized at the restricted Hartree-Fock *ab initio* theory using the 3-21G basis set. This basis considers that a first row atom has three shells. One is an *s*-shell composed of 3 primitive gaussian functions, the second shell is a combination of 2 primitive *sp*-shells, while the third shell consists of a single function. The input structure was the geometry optimized by the AM1 program [8]. The linear α and quadratic β tensor components were calculated analytically *via* electric field derivatives of the total energy

$$E(F) = E^\circ - \sum_i \mu_i F_i - \frac{1}{2} \sum_{i,j} \alpha_{ij} F_i F_j - \frac{1}{6} \sum_{i,j,k} \beta_{ijk} F_i F_j F_k$$

The α polarizability is expressed as a mean value

$$\langle \alpha \rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$
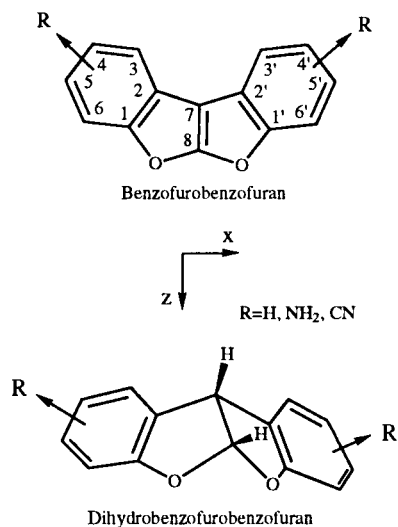

Figure 1. Molecular structure and numbering of benzofurobenzofurans.

The β hyperpolarizability is expressed in term of

$$\beta_v = (\beta_X^2 + \beta_y^2 + \beta_Z^2)^{1/2} \ , \quad \beta_i = \sum_j \beta_{ijj} \ , \quad i,j = x,y,z$$

as well as in terms of [9]

$$\beta_\mu = \frac{\beta \cdot \mu}{\|\mu\|} = \frac{\sum\limits_{i,j} \beta_{ijj}\mu_i}{\left(\sum\limits_i \mu_i^2\right)^{1/2}}$$

where the β_μ is aligned to lie along the direction of the molecular dipole moment μ. It is well known that calculation of accurate (hyper)polarizability values requires the use of extended basis set supplemented by polarization and diffuse functions, as well as the inclusion of electron correlation energy. For medium-sized molecules a split valence basis set such as a 3-21G or 6-31G augmented by a diffuse p or d functions on the heavy atoms, may give satisfactory results, especially when the main purpose is to establish trends within series of compounds rather than to predict absolute values [9-15]. In the present work the molecular properties were calculated by the 3-21G and 3-21G(+p) basis sets. The latter adds a diffuse p function to the heavy atoms. The p exponent (0.075) is the one previously optimized for hyperpolarizability calculations on push-pull amino-nitro polyenes [10]. Note that the bare 3-21G basis was recently proved to give satisfactory description of (hyper)polarizability properties of some medium-sized molecules [9,16,17].

Excited state properties were calculated by the AM1 program. Single excited configurations were built by the upper ten occupied and the lower ten unoccupied levels. *Ab initio* calculations were carried out with the GAUSSIAN 92 suite of programs [18].

Results and Discussion.

Molecular Structures.

The calculated RHF/3-21G molecular structures of the studied compounds are reported in Tables 1 and 2. Table 2 also shows the experimental X-ray structure of dihydrobenzofurobenzofuran [19] for comparison. Stationary points on the potential energy surface were tested by vibrational analysis. Benzofurobenzofuran compounds are planar, except the 3,3'-derivatives, which, owing to steric interactions, adopt a slightly non planar geometry: in the 3,3'-NH₂ derivative the amino groups have the distal N-H bonds coplanar with the ring system, while the vicinal N-H bonds show a dihedral H-N-C_i-C_j angle of 34°; in the 3,3'-CN derivative the C_i-C≡N group is no longer linear and coplanar with the ring system, showing a C_i-C≡N angle of 174.8° and a N≡C-C_i-C_j dihedral angle of 16.5°. The molecular geometry of the benzofurobenzofuran framework is quite rigid, being only very slightly affected by the substitution. AM1 calculations give similar geometries, the main difference being encountered in the C_7-C_8 distance, which in the unsubstituted compound is predicted to be 0.073Å longer than in the 3-21G calculations.

Table 1

Calculated Restricted Hartree-Fock/3-21G Geometries of Benzofurobenzofuran Derivatives

Substituent	3,3'-H	3,3'-NH₂	4,4'-NH₂	5,5'-NH₂	6,6'-NH₂	3,3'-CN	4,4'-CN	5,5'-CN	6,6'-CN
C_1-C_2	1.403	1.400	1.401	1.401	1.395	1.409	1.405	1.405	1.402
C_2-C_3	1.384	1.393	1.381	1.383	1.387	1.394	1.380	1.385	1.383
C_3-C_4	1.385	1.392	1.396	1.381	1.384	1.396	1.391	1.380	1.385
C_4-C_5	1.391	1.389	1.402	1.404	1.390	1.383	1.397	1.398	1.388
C_5-C_6	1.386	1.382	1.383	1.394	1.396	1.384	1.382	1.391	1.391
C_1-C_6	1.368	1.371	1.365	1.367	1.378	1.363	1.368	1.363	1.373
C_2-C_7	1.455	1.466	1.453	1.459	1.456	1.475	1.455	1.450	1.455
C_7-C_8	1.342	1.341	1.347	1.336	1.344	1.351	1.342	1.347	1.341
C_1-O	1.417	1.408	1.425	1.408	1.426	1.408	1.409	1.415	1.404
C_8-O	1.347	1.348	1.342	1.357	1.345	1.334	1.347	1.342	1.349
N-H		1.000	0.994	0.995	0.995				
C-N		1.388	1.378	1.376	1.367	1.139	1.141	1.140	1.139
C_i-C						1.424	1.427	1.429	1.423
∠C_1-C_2-C_3	118.5	118.8	119.2	117.6	119.0	116.2	118.8	118.5	118.8
∠C_2-C_3-C_4	118.6	117.2	119.3	119.4	117.2	119.0	118.4	118.7	118.7
∠C_3-C_4-C_5	121.4	122.2	119.6	122.0	122.5	122.2	121.5	121.4	121.5
∠C_4-C_5-C_6	120.9	121.4	121.6	119.0	121.5	120.0	120.7	120.9	120.8
∠C_1-C_6-C_5	116.8	115.8	117.6	117.7	114.6	117.0	117.0	116.6	116.8
∠C_1-C_2-C_7	105.0	105.3	104.9	105.1	104.6	104.8	104.9	105.0	104.7
∠C_2-C_7-C_8	105.3	104.5	105.4	105.1	105.6	103.9	105.2	105.3	105.3
∠C_7-C_8-O	115.7	115.9	115.7	115.6	115.7	116.7	115.6	115.6	115.5
∠C_1-O-C_8	103.6	103.9	103.4	103.5	103.1	103.9	103.8	103.7	103.7
∠H-N-H		115.3	118.1	118.1	119.0				
∠C-N-H		118.2	121.0	120.9	121.1				

Table 2

Calculated Restricted Hartree-Fock/3-21G Geometries of Dihydrobenzofurobenzofuran Derivatives

Substituent	3,3'-H	3,3'-H exp [a]	3,3'-NH$_2$ [b]	4,4'-NH$_2$	5,5'-NH$_2$	6,6'-NH$_2$	3,3'-CN [b]	4,4'-CN	5,5'-CN	6,6'-CN
C_1-C_2	1.379	1.391	1.418	1.374	1.379	1.366	1.422	1.382	1.379	1.380
C_2-C_3	1.375	1.398	1.402	1.374	1.374	1.382	1.390	1.370	1.375	1.371
C_3-C_4	1.389	1.397	1.425	1.398	1.385	1.384	1.413	1.396	1.387	1.393
C_4-C_5	1.385	1.393	1.386	1.395	1.398	1.387	1.390	1.391	1.389	1.379
C_5-C_6	1.387	1.413	1.400	1.385	1.399	1.392	1.400	1.383	1.393	1.396
C_1-C_6	1.372	1.378	1.386	1.370	1.368	1.384	1.387	1.374	1.370	1.375
C_2-C_7	1.514	1.521	1.500	1.514	1.514	1.516	1.501	1.515	1.514	1.516
C_7-C_8	1.583	1.583	1.587	1.585	1.583	1.585	1.588	1.583	1.584	1.583
C_1-O	1.384	1.402	1.390	1.391	1.381	1.395	1.389	1.375	1.379	1.370
C_8-O	1.432	1.438	1.435	1.431	1.434	1.432	1.435	1.433	1.432	1.434
N-H			0.997	0.994	0.994	0.995				
C-N			1.398	1.382	1.373	1.371	1.163	1.141	1.140	1.139
C_i-C							1.421	1.427	1.429	1.423
∠C_1-C_2-C_3	119.9	119.9	118.7	120.7	118.6	120.4	118.0	120.0	120.0	120.1
∠C_2-C_3-C_4	119.0	117.8	117.5	119.6	119.9	117.5	119.0	118.8	119.0	119.0
∠C_3-C_4-C_5	120.2	121.5	121.5	118.5	120.9	121.5	121.3	120.3	120.1	120.3
∠C_4-C_5-C_6	120.9	120.9	121.6	121.6	119.0	121.3	121.0	120.8	121.1	120.8
∠C_1-C_6-C_5	117.6	116.4	116.4	118.4	118.3	115.6	116.9	117.7	117.3	117.6
∠C_1-C_2-C_7	109.2	109.1	108.8	109.1	109.6	108.8	108.5	109.2	109.1	108.9
∠C_2-C_7-C_8	101.7	101.4	101.2	101.8	101.3	102.0	101.4	101.6	101.7	101.7
∠C_7-C_8-O	106.6	107.6	108.6	106.7	106.8	106.6	108.6	106.5	106.4	106.3
∠C_1-O-C_8	109.8	108.5	107.8	109.3	109.6	108.9	107.7	110.0	109.9	109.9
∠H-N-H			112.5	118.1	118.1	119.4				
∠C-N-H			113.6	121.0	120.9	121.4				
w [c]	117.1	116.6	117.8	117.5	117.5	117.3	117.5	116.8	116.8	116.8

[a] X-Ray diffraction, ref [19]. [b] From AM1 calculations. [c] Dihedral angle between the two dihydrobenzofuran planes. Dihedral angles of the 3,3'-substituent: 3,3'-NH$_2$, H_{prox}N-C_3-C_2 = 48°, H_{dist}-N-C_3-C_4 = -6°; 3,3'-CN, N-C-C_3-C_2 = 150°, N-C-C_3 = 175.5°.

Hydrogenation of the C_7=C_8 bond produces the expected lengthening of this bond and relevant structural variation in the heterocycle ring. The molecule is no longer planar but has a V-shaped form with a dihedral angle between the two dihydrobenzofuran units of 117.1°, which compares well with the experimental value of 116.5° in the solid [19]. Also the dihydrobenzofurobenzofuran structure is quite unaffected by the substitution. The structure of the 3,3'-diamino- and 3,3'-dicyano-derivatives were obtained by AM1 calculations, owing to convergence problems in the *ab initio* calculations. On the other hand it was recently shown [16], and also verified in the present work, that the 3-21G β values calculated on the

AM1 geometries are very close to those obtained by the full *ab initio* procedure.

Electronic Properties and (Hyper)polarizabilities.

Table 3 shows the π charge distribution of benzofurobenzofuran derivatives, while Table 4 reports the calculated AM1 lowest energy singlet electronic transitions of both series of compounds together with excited state dipole moments. Dipole moments, polarizabilities α and hyperpolarizabilities β are shown in Table 5. The π charge distribution indicates that in the unsubstituted benzofurobenzofuran molecule the furan ring behaves as a π-electron donor with respect to the benzene ring. This feature is maintained even when the benzene ring brings the strong π-electron donor NH$_2$ group, except in the case of the 3,3'-NH$_2$ derivative. The cyano group further facilitates the π-electron flux from the furan to the benzene ring.

Ground state dipole moments were calculated at both the semi-empirical AM1 and *ab initio* 3-21G level. The AM1 μ are claimed to be close to the experimental values [20], while the 3-21G theory is known to give somewhat higher values. We note that the dipole moment of the prototype molecule *p*-nitroaniline is calculated to be 7.32 and 7.79 D at AM1 and 3-21G level, respectively, compared with an experimental value in benzene solution of 6.29 D [21]. The two sets of μ data show the same trend. The dipole moment

Table 3

Calculated 3-21G Mulliken π Charge Densities of Benzofurobenzofuran Derivatives

Substituent	q_π (benzene)	q_π (furan)	q_π (R)
3,3'-H	-0.091	0.091	
3,3'-NH$_2$	-0.176	-0.094	0.270
4,4'-NH$_2$	-0.211	0.073	0.138
5,5'-NH$_2$	-0.201	0.059	0.142
6,6'-NH$_2$	-0.200	0.049	0.151
3,3'-CN	-0.081	0.111	-0.030
4,4'-CN	-0.074	0.108	-0.033
5,5'-CN	-0.076	0.110	-0.034
6,6'-CN	-0.083	0.108	-0.025

Table 4

AM1 Most Intense Lowest Vertical Singlet Electronic Transitions (ΔE, nm), Oscillator Strength (f), Excited State Dipole Moment (μ_e. Debye) and Dipole Moment Change Between Excited and Ground State ($\Delta\mu_{eg}$, Debye) of Benzofurobenzofuran and Dihydrobenzofurobenzofuran Derivatives

| Substituent | Benzofurobenzofuran | | | | Dihydrobenzofurobenzofuran | | | |
	ΔE	f	μ_e	$\Delta\mu_{eg}$	ΔE	f	μ_e	$\Delta\mu_{eg}$
3,3'-H	307	0.14	0.17	-1.56	321	0.02	1.60	-0.89
	249	1.22	0.77	-0.96	219	1.21	1.74	-0.75
	227	0.12	1.00	-0.73	216	0.16	2.04	-0.45
	223	0.16	0.15	-1.58	203	0.47	1.44	-1.05
3,3'-NH$_2$	255	1.08	3.34	-0.54	314	0.04	4.94	0.46
	244	0.15	4.83	0.95	240	1.03	4.71	0.23
	235	0.29	5.44	1.56	228	0.21	12.03	7.55
	219	0.22	6.19	2.31	225	0.58	4.34	-0.14
4,4'-NH$_2$	276	1.50	4.10	-0.22	317	0.19	5.85	0.72
	262	0.35	7.25	2.93	231	0.73	6.75	1.62
	239	0.12	7.52	3.20	217	0.19	6.46	1.33
	233	0.82	5.99	1.67	208	1.41	6.95	1.82
5,5'-NH$_2$	336	0.52	1.05	-1.03	325	0.13	3.03	0.43
	251	1.26	1.65	-0.38	235	1.07	2.04	-0.56
	221	0.70	1.83	-0.19	226	0.42	1.94	-0.66
	214	0.51	0.16	-1.87	219	0.36	4.94	2.34
6,6'-NH$_2$	266	0.75	2.01	0.55	317	0.07	2.30	1.78
	235	0.28	2.84	1.38	240	0.91	2.76	2.24
	230	0.31	1.84	0.38	216	1.36	3.24	2.72
	210	0.30	2.11	0.65	214	0.51	3.17	2.65
3,3'-CN	253	1.32	5.03	1.07	337	0.04	4.46	1.27
	235	0.21	5.35	1.39	235	0.15	4.30	1.11
	227	0.27	3.21	-0.75	226	1.10	3.65	0.46
	225	0.11	2.64	-1.32	212	1.19	5.23	2.04
4,4'-CN	257	1.59	5.02	1.39	317	0.03	4.52	0.41
	250	0.14	2.31	-1.32	299	0.17	4.59	0.48
	228	0.56	6.59	2.96	227	1.35	5.12	1.01
	223	0.23	2.02	-1.61	203	1.89	5.72	1.61
5,5'-CN	316	0.35	0.92	-0.70	325	0.05	4.26	-0.29
	247	1.19	0.81	-0.81	228	1.34	4.44	-0.11
	232	0.37	1.70	0.08	218	0.31	4.17	-0.38
	223	0.64	0.13	-1.49	203	1.23	4.93	0.38
6,6'-CN	256	1.66	6.39	-0.57	323	0.06	6.66	-1.29
	226	0.35	5.00	-1.96	225	1.19	8.02	0.07
	216	0.25	7.16	0.20	223	0.16	7.41	-0.54
	209	0.29	6.92	-0.04	206	1.98	7.83	-01.2

of the unsubstituted molecules are already substantial, with μ-dihydrobenzofurobenzofuran higher than μ-benzofurobenzofuran, essentially owing to the inversion in the C_1-O and C_8-O bond lengths on passing from benzofurobenzofuran to dihydrobenzofurobenzofuran and a consequent narrowing of the angle between the two furan dipole moment vectors. The dipole moment of substituted compounds obviously depends on the substituent position, the largest value being obtained in both the series of compounds for the 4,4' and 6,6' substitution in the amino- and cyano-derivative, respectively. The latter is predicted to be the present highest polar compound. The dipole moments of the dihydrobenzofurobenzofuran series remain higher than those of the benzofurobenzofuran series. A remarkable effect of the molecular structure on μ is found in the 5,5'-CN derivative (Table 5), which in the dihydrobenzo-

furobenzofuran series is more than twice higher than in the benzofurobenzofuran series. The addition of p diffusion functions to the 3-21G basis increases the dipole moment value in both series of compounds, the largest effect being encountered in the 6,6'-CN derivatives where μ increases by about 1D. A dipole moment analysis can be usefully applied to investigate possible electronic interactions between the two benzofuran frameworks in benzofurobenzofuran. To this end the dipole moment of the monosubstituted 6-NH$_2$ and 6-CN compounds were computed to abstract the C-NH$_2$ and C-CN group moment, which were found to be 1.55 and 3.78 D, respectively, at the 3-21G level on the AM1 geometry. A simple vector addition of group moments gives for the 6,6'-NH$_2$ derivative $\mu = 0.71$ D, vs. a calculated value of the entire molecule of 0.73 D. The corresponding figures for the 6,6'-CN derivative are

9.95 and 9.86 D. The same procedure, when applied to 6-NH$_2$,6'-CN-benzofurobenzofuran gives μ(vectorial sum) = 4.31 D *vs.* μ(calc) = 4.33 D. The same results are

tron transfer. However the dipole moment change $\Delta\mu_{eg}$ is maintained rather small, indicating a modest charge transfer on excitation. The influence of the cyano-group on the

Table 5

Calculated Dipole Moments μ (Debyes), Mean Polarizability <α> (a.u.) and Hyperpolarizability β (a.u.) of Benzofurobenzofuran and Dihydrobenzofurobenzofuran Derivatives

	Benzofurobenzofuran (3-21G)				Benzofurobenzofuran (3-21G+p)			
Substituent	μ	<α>	β_v	β_μ	μ	<α>	β_v	β_μ
3,3'-H	2.39	122	286	-286	2.79	142	337	-337
3,3'-NH$_2$	4.58	135	43	43	4.66	158	46	46
4,4'-NH$_2$	4.90	137	103	103	4.88	161	37	37
5,5'-NH$_2$	2.69	139	344	-344	3.07	162	387	-387
6,6'-NH$_2$	0.84	137	548	548	0.02	160	623	623
3,3'-CN	5.51	147	241	241	5.81	170	401	401
4,4'-CN	5.14	150	308	308	5.54	175	561	561
5,5'-CN	2.34	158	380	-380	2.69	182	441	-441
6,6'-CN	9.82	150	397	-397	10.87	175	316	-316

	Dihydrobenzofurobenzofuran (3-21G)				Dihydrobenzofurobenzofuran (3-21G+p)			
Substituent	μ	<α>	β_v	β_μ	μ	<α>	β_v	β_μ
3,3'-H	3.18	118	165	-160	3.58	121	185	-173
3,3'-NH$_2$	5.54	135	81	22	5.61	158	93	40
4,4'-NH$_2$	5.75	132	364	353	5.74	155	202	188
5,5'-NH$_2$	3.20	134	370	-64	3.54	157	361	7
6,6'-NH$_2$	0.09	131	503	454	0.91	155	584	565
3,3'-CN	4.69	148	139	122	5.03	171	269	239
4,4'-CN	5.87	146	254	222	6.38	169	499	468
5,5'-CN	6.15	148	132	58	6.82	172	231	68
6,6'-CN	10.89	145	247	-237	11.99	169	153	-110

expected to be found also in the dihydrobenzofurobenzofuran series. They clearly indicate that the substituent groups in the two benzofuran moieties are practically noninteracting, which is of relevance in determining the optical and nonlinear optical properties of the present compounds.

In a two-state model approximation [22] β is essentially determined by the dominant charge transfer electronic transition and the associated transition moment and dipole moment change ($\Delta\mu_{eg}$). In a more complete description of hyperpolarizability, all excited states may contribute to β. Table 4 shows that the unsubstituted benzofurobenzofuran compound is characterized by a strong absorption at 249 nm (f = 1.22) arising from a HOMO→LUMO+1 transition. It is of charge transfer type involving electron migration from the furan to the benzene ring. The associated dipole moment acts in opposite direction with respect to the ground state, as happens also for the other excited states, so a negative β value is expected for this compound. The corresponding charge transfer transition in benzofuran is calculated at 246 nm (f = 0.33), which compares well with the experimental absorption in ethene solution at 241 nm (f = 0.2) [23]. The charge transfer transition is moderately shifted bathochromically in the amino derivatives, where it contains also a NH$_2$→benzene elec-

charge transfer transition is less pronounced, although $\Delta\mu_{eg}$ values are somewhat higher. The loss of planarity and symmetry in the dihydrobenzofurobenzofuran compounds involves a σ-π mixing and the presence of several allowed transitions with comparable intensity. The most intense transition in the unsubstituted compound is now found at higher energy than in the planar compound and has a mixed charge transfer and locally excited character. The effect of substitution in the dihydrobenzofurobenzofuran series is similar to that in the benzofurobenzofuran series. It is worth noting that in both series of compounds all the electronic transitions produce small $\Delta\mu_{eg}$ values, thus this term is not very effective in determining β, which will essentially depend on the energy and intensity of the electronic transition.

As far as (hyper)polarizabilities are concerned, a noticeable effect can first be noted on both α and β values of the added diffuse *p* function to the 3-21G basis. In some cases β is more than doubled. These results stress the necessity of using diffused basis sets also in molecular systems of the actual size. The average first order polarizabilities are calculated to be all of the same order of magnitude, as expected, <α> depending essentially on the molecular size, while only minor variations are associated with the

substituent position. For comparison we note that the present $<\alpha>$ values are about two times greater than $<\alpha>$ of *para*-nitroaniline (86.7 a.u.) calculated with the same 3-21 G(+p) basis. By contrast β_μ, as a vector quantity, depends on the molecular geometry and on the substituent position. β_μ also depends on the angle θ between the μ and β_v, so that $\beta_\mu\cdot\mu$ vanishes when θ comes close to 90°. In the benzofurobenzofuran series, owing to the C_{2v} molecular symmetry, β_v lies along the μ axis. Within the present series of compounds β_v values differs by more than one order of magnitude, the highest value being displayed in both the series by the 6,6'-NH_2 derivatives, reaching about 60% β_v of *para*-nitroaniline (976 a.u.), calculated with the same 3-21G(+p) basis. The relatively large β_v value of these compounds can be accounted for by considering that the dominant electronic transitions are associated with the present highest $\Delta\mu_{eg}$ values, which in turn are related to their small ground state dipole moment. By contrast 3,3'- and 4,4'-NH_2 derivatives have rather low β_v values owing to opposing effects of the transversal component of β_i, as well as to very small $\Delta\mu_{eg}$ values. Based on the $\Delta\mu_{eg}$ values associated to the dominant charge transfer transition, the amino derivatives of benzofurobenzofuran series, but the 6,6'-one, should display negative β_μ values. Actually this happens only for 5,5'-NH_2-benzofurobenzofuran, indicating that the simple two-state model is here not generally applicable. Benzofurobenzofuran cyano-derivatives show rather homogeneous β_μ values and appear to follow the two-state model. In agreement with the results of the dipole moment analysis, the substituent groups in the two benzofuran moieties behave as noninteracting units in determining the intrinsic hyperpolarizability value. In fact β_v of 6-NH_2,6'-CN-benzofurobenzofuran (630 a.u., 3-21G) may be reproduced by vector sum of the β vector components of 6-NH_2-benzofurobenzofuran (β_z = -453, β_x = 234 a.u.), 6-CN-benzofurobenzofuran (β_z = -376, β_x = 118 a.u.) and benzofurobenzofuran (β_z = -286 Table 5), which gives β = 645 a.u.. The compounds of the dihydrobenzofurobenzofuran series show somewhat smaller β values than the corresponding ones in the benzofurobenzofuran series. This can be essentially traced back to a smaller $\Delta\mu_{eg}$ value. Dihydrobenzofurobenzofuran derivatives, however, display better transparency in the near ultraviolet spectral region.

As a conclusion, in relation to the suitability of the present compounds for nonlinear optical applications, one can notice that, although the isolated molecules show a relatively modest hyperpolarizability value, they are predicted to have a good transparency in the visible region, which is very probably maintained in the polymer, substituent groups in the two benzofuran moieties being electronic noninteracting units. Notice that dihydrobenzofurobenzofuran crystals are colorless [19]. The hyperpolarizability of high-order oligomers or poly-

mers is thus expected to be simply defined by the relative orientations of the oligomers, resulting from simple β_μ, addition for uniformly oriented oligomers. Both benzofurobenzofurans and dihydrobenzofurobenzofurans are conformationally rigid compounds with quite stable structure towards the substitution. Some derivative, such as 6,6'-cyano, shows an exceptionally high polarity with appreciable β_μ value. Its use in poled polymers is thus of interest, being expected to be very easily orientable by an external electric field.

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