Electrostatic properties of cyano-containing mesogens

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We analyse the electrostatic properties of a set of cyano-containing mesogen molecules with different rigid cores and variable alkyl chain lengths, computing the molecular charge distributions. Using the simple prototype benzonitrile, we analyse the reliability of the quantum chemical methods used to estimate the electrostatic dipole moments of polar conjugated molecules. We show that the electronic properties of the long mesogenic molecules can be treated by combining HF geometry optimization procedures with single point MP2 calculations. We compare the results of these computations with the available experimental phase transition data of mesogens and discuss some examples of how the non-trivial mesomorphic behaviour, which is usually observed in these cyano compounds, can be qualitatively explained by the molecular electrostatic interaction potential.

1. Introduction

Electrostatic interactions play a particularly important role in mesogenic systems. For example they give rise to a variety of smectic phases. The differences in molecular ordering of smectic A_1, A_2 and A_d phases have been explained solely by molecular dipole interactions [1]. It is expected that the specific charge distributions in molecules play a decisive role in the formation of ferro-electric, antiferroelectric and ferrielectric smectic phases [2, 3]. Molecular polarity leads to the appearance of phenomena such as flexo- and ferro-electricity or electro-clinic behaviour [4]. Even in the less ordered nematic mesophase, phenomena like induced smectic ordering or re-entrant phase behaviour appear due to electrostatic interactions [5]. Nevertheless, little is known about the electrostatic properties of mesogen molecules. Experimental methods usually deliver information about the total dipole moment of the molecule, but not about the charge distribution and as a consequence very little information is gained about local electrostatic interactions.

Quantum chemical computations can in principle yield more detailed information, but they are still restricted by the contemporary computer power due to the rather large size of the mesogen molecules. Therefore semi-empirical approaches or low level *ab initio* computations are often used for calculations of molecular properties. In such cases the calculated molecular dipole moments often deviate strongly from the experimental

values. Before we determine the distribution of partial charges, we examine at which level of approximation and to what extent the computational approach can be sufficiently reliable for mesogens. We used several homologous sets of typical mesogens containing a cyano fragment as a basis for our studies. This particular set has been chosen because cyano compounds are constituents of hundreds of industrial liquid crystal mixtures. In an initial step, we check our methods on the more simple prototype benzonitrile. Finally we compare the results of the computations with available experimental data on mesogens. The partial charges obtained can be used subsequently for reliable computer simulation studies.

2. Computational method

For all quantum chemical calculations we use the program package GAUSSIAN 94 [6], and we always perform first a Hartree–Fock (HF) geometry optimization which is followed by an electronic structure analysis. If not otherwise mentioned, the standard 6-31G* split valence basis set is used. Unfortunately it is not possible to compare all computer data with experimental results. What can be compared frequently are geometrical parameters and computed dipole moments. Despite the vectorial character of the dipole moment, most experimental data furnish only its magnitude. It is well known (see for example [7]) that even near the HF limit, the magnitudes of dipole moments are usually in error by a few tenths of a debye. As can be seen in table 1, the calculated dipole moments for molecules without the

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Table 1.   Calculated and experimental dipole moments in Debye. The calculations were performed using the 6-31G* basis set.

Molecule	Method	Calculated	Exp.
HCN	HF//HF	3.21	2.957 ± 0.025 [8]
	MP2//HF	2.96	2.99 [7]
	MP2//MP2	2.95	
CH$_3$CN	HF//HF	4.04	3.97 [9]
	MP2//HF	3.75	3.44 [10]
	MP2//MP2	3.76	3.913 ± 0.002 [11]
1-Phenyl-4-methylbenzene	HF//HF	0.36	0.33 [12]–0.37 [13]
	MP2//MP2	0.37	
1-Phenyl-4-methylcyclohexane	HF//HF	0.27	—
	MP2//MP2	0.28	

terminal cyano group are well described by HF calculations. In agreement with previous observations [7] the dipole moment of the cyano fragment is overestimated by about 10% on the HF level. For such polar molecules, it is necessary to account for electron correlation, and for this we use Møller–Plesset perturbation theory of 2nd order. When using this approach, we perform single point calculations for the HF optimized structures, labelled as MP2/6-31G*//HF/6-31G*. For all molecules that are not too large, the geometry optimization too is performed on this level (MP2/6-31G*//MP2/6-31G*).

In table 1, one can see clearly the effect of including electron correlation on the magnitude of the calculated dipole moments. The moments of the molecules containing the terminating CN group are lowered by about 10%, while for the non-polar fragments they are nearly unchanged.

The electrostatic properties are calculated from the density matrix. A visualization of the quantum mechanically calculated electrostatic potential (ESP) for different mesogens with short alkyl chains (see figure 1) is shown in figure 2. These pictures show the ESP on a

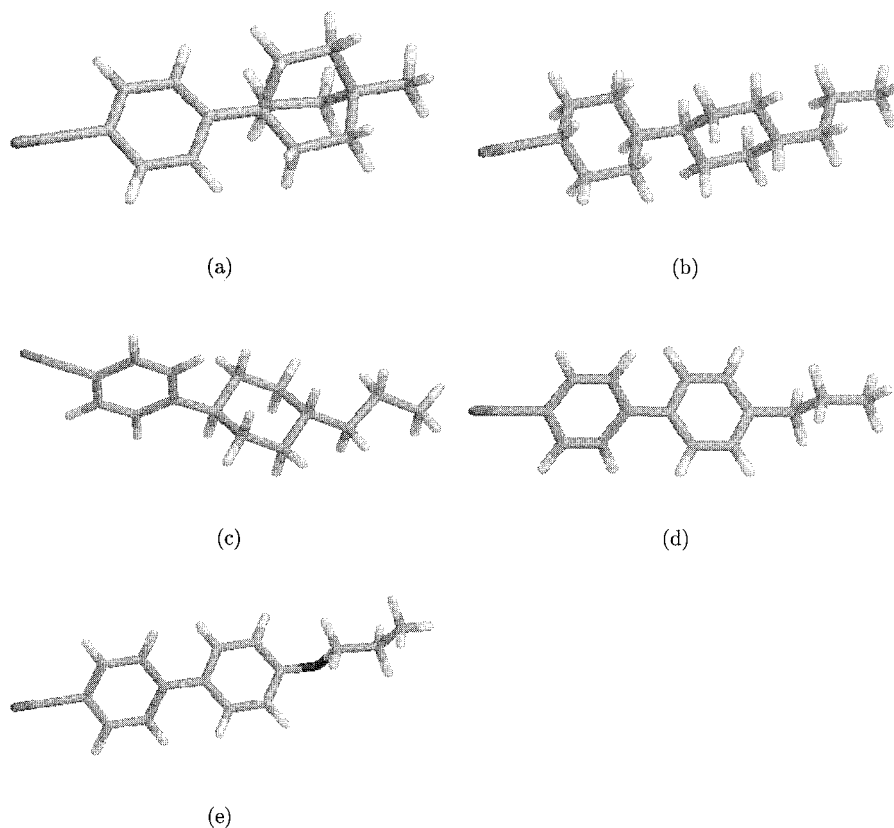(a)   (b)

(c)   (d)

(e)

Figure 1.   Models of 1BCO (*a*), 3CCH (*b*), 3PCH (*c*), 3CB (*d*) and 3OCB (*e*). Note that the structure shown for 3OCB represents a local minimum of the energy.
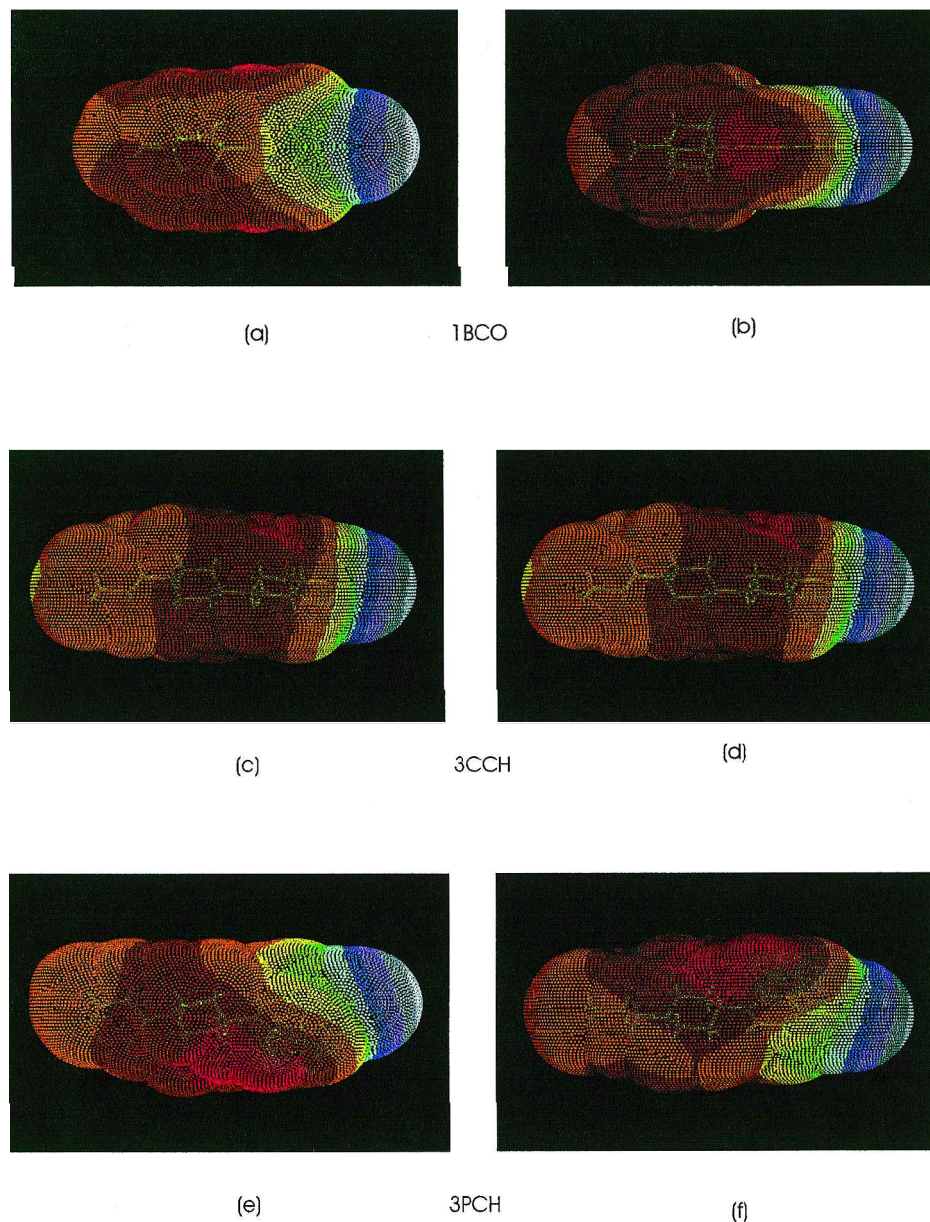
(a)   1BCO   (b)

(c)   3CCH   (d)

(e)   3PCH   (f)

Figure 2.   ESP surfaces for 1BCO, (*a*) and (*b*); 3CCH (*c*) and (*d*); 3PCH (*e*) and (*f*); 3CB (*g*) and (*h*); and 3OCB (*i*) and (*j*). The calculations were performed using the MP2/6-31G*//HF/6-31G* method. The surfaces shown are 2.0 Å above the van der Waals surfaces of the molecules. Each molecule is shown in two perspectives, rotated by 90°, (*a–f*), or 180°, (*g–j*) (see figure 2 continued). In (*k*) the colour coding for the electrostatic potential surfaces is shown. Each colour belongs to a different interval of potential energy of a test charge of 1 |*e*|.

surface that is 2 Å away from the van der Waals surface. For this purpose the potential energy of a positive test charge (1 |*e*|) was calculated at about 13 000 points on this surface. The potential energy intervals that belong to the different colours are defined in figure 2 (*k*). Each molecule in figure 2 is shown in two different perspectives.

To parametrize the inter- and intra-molecular interactions for computer simulations or force field calculations, we determine atom positioned partial charges as follows. To reproduce the electrostatic potential in the surroundings of the molecule calculated from the electron density, we determine values for the q_i from ESP fits to the *ab initio* data. We calculate the ESP at 14 surfaces with a constant distance to the van der Waals surface of 1.0, 1.2, … , 3.6 Å. On each surface about 2000 points were generated, exhibiting a constant point density. We apply symmetry constraints to obtain equal values of point charges on conformationally different, but topologically equivalent sites. The RESP program [14] is used, applying weak hyperbolic restraints of
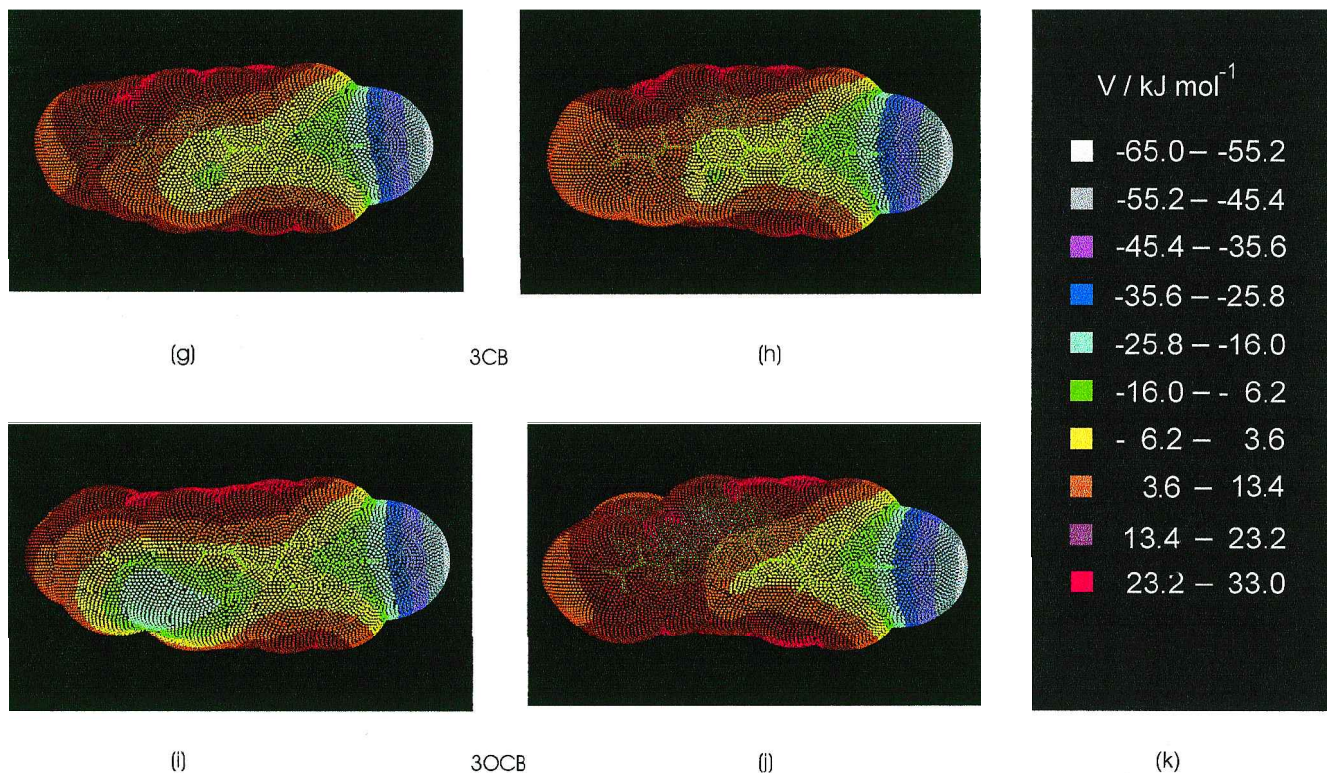
Figure 2. (*continued*).

about 5.0×10^{-4} au to the fit to reduce the resulting partial charges. The use of charge restraints and symmetry constraints does not affect the quality of the fit substantially. This is shown in table 2, where the resulting dipole moments of different charge models for 5PCH are compared. For this purpose we made:

(i) a fit with point charges on each atomic site without additional constraints;
(ii) a fit applying weak hyberbolic charge restraints of 5.0×10^{-4} au;
(iii) a fit applying weak hyperbolic charge restraints and symmetry constraints as we used in our simulations.

Table 2. Comparison of different charge models for 5PCH. The RRMS is defined in equations (1) and (2). The resulting charges on the heavy atoms for the different fitting procedures can be seen in figure 3.

Model	Dipole moment/D	RRMS of ESP fit
HF/6-31G*	5.719	—
Unconstrained fit	5.716	0.0688
Fit with charge restraints	5.706	0.0725
Fit with charge restraints and symmetry constraints	5.706	0.0768

In table 2 we also list the relative root mean square deviation (*RRMS*) which is defined as

$$RRMS \equiv \left(\chi^2_{esp} \Big/ \sum_i \hat{V}_i^2 \right)^{1/2} \qquad (1)$$

$$\chi^2_{esp} = \sum_i (V_i^{qm} - \hat{V}_i)^2. \qquad (2)$$

In equation (2) the quantum mechanical ESP at location r_i is represented by V_i^{qm} and the point charge ESP is given by $\hat{V}_i$. The resulting charges on the heavy atoms of 5PCH are plotted in figure 3. The partial charges for all substances studied in this paper can be obtained from the authors.

3. Discussion

3.1. *Benzonitrile*

To choose a reliable method for calculating the electrostatic properties we made a series of computations on benzonitrile. Concerning the charge distribution, this is the most subtle molecule fragment for a great variety of mesogens. The optimization of the molecular geometry was performed with different methods (HF or MP2) and basis sets. As seen from table 3, all these methods reproduce the molecular geometry with good accuracy. All variations of bond lengths occur in the range ± 2.5 pm. In figure 4 we show the dependence of the benzonitrile dipole moment on the length of the cyano bond to
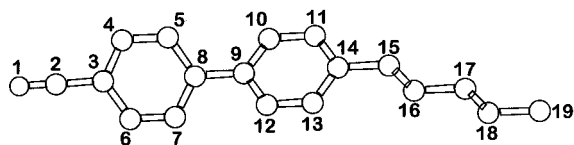
(a)
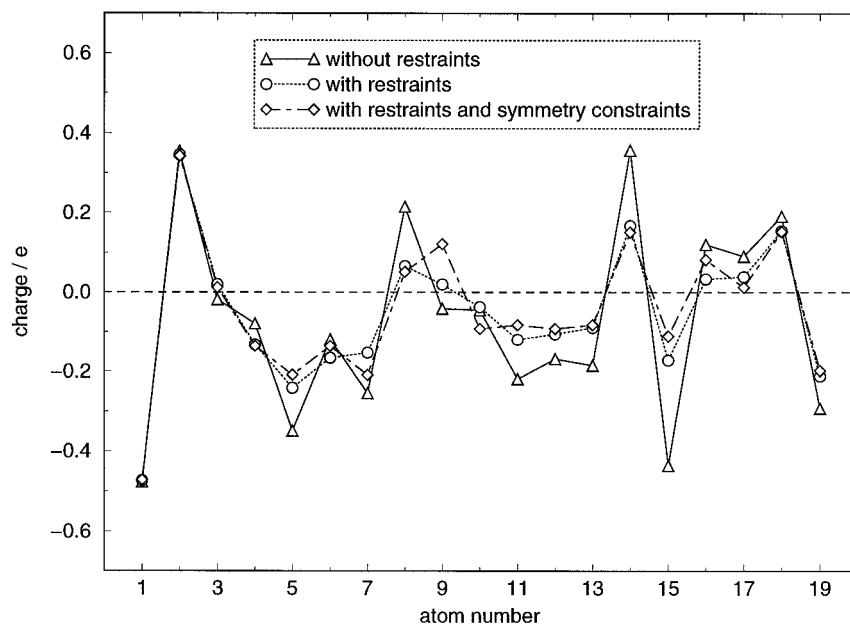
(b)

Figure 3. (*a*) The numbering scheme of the heavy atoms for all mesogens (except 5OCB) containing pentyl chains. (*b*) Partial charges of the heavy atoms of 5PCH obtained by fitting the electrostatic potential without constraints, with weak restraints and with constraints to take molecular symmetry into account (charges of the hydrogen atoms are not shown). All calculations were done using the HF/6-31G* wave function.

Table 3. Some geometric parameters of benzonitrile obtained with different methods using different basis sets. In the first line, experimental values from [15] are given. r_{CN} is the length of the cyano bond, r_{CC} is the CC bond length between the carbons of the cyano group and the phenyl ring, and r_{CC}^{benz} is the CC length in the phenyl ring near the cyano group. CCC measures the CCC angle in the phenyl ring near the cyano group.

Method	Basis set	r_{CN}/pm	r_{CC}/pm	r_{CC}^{benz}/pm	CCC/°
(Exp.		115.9	144.5	139.1	118.75)
HF	STO-3G	115.7	146.3	139.5	120.02
HF	3-21G	114.0	142.9	138.9	119.95
HF	6-31G*	113.7	144.5	139.1	119.78
MP2	6-31G*	118.4	143.6	140.3	119.70
MP2	6-31 + G*	118.5	143.7	140.5	119.68

which the dipole moment is most sensitive. For this purpose we first calculated the optimized HF/6-31G* and MP/6-31G* structures. After this we varied exclusively

the N–C bond length, leaving the other geometric parameters unchanged (i.e. no further geometry optimization was performed). As one can see, variations of the geometry within the range of table 3 change the calculated value of the dipole moment only by about 0.1 D (HF) or even less than 0.02 D (MP2). This is far beyond the precision of dipole moment calculations of such strongly polar molecules as benzonitrile. So we conclude that geometry parameters have a minor effect on the results of the dipole moment calculations (at least if they are varied within the limits delivered by different *ab initio* methods and basis sets). In table 4 we present dipole moments calculated with different methods (geometry optimized with the same method). The results show that for this molecule HF/3-21G calculations reproduce the experimental value fairly well. The larger the basis set the worse is the agreement. The same tendency is observed within the MP2 level, but the resulting values are very close (maximal deviation of 6%) to the experimental ones. So we conclude that for cyano derivatives
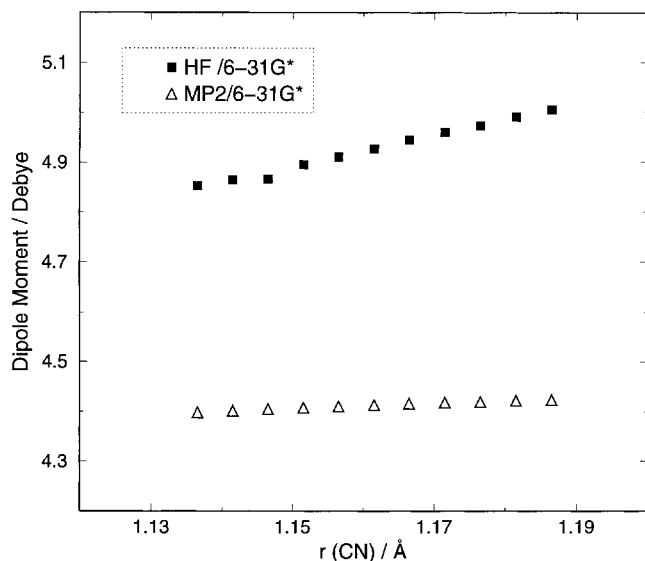
Figure 4. Dependence of the dipole moment of benzonitrile on the length of the cyano bond calculated with HF/6-31G* and MP2/6-31G*. In these calculations the cyano bond was varied while the rest of the molecule was fixed in the fully optimized HF/6-31G* or MP2/6-31G* structure.

Table 4. Dipole moments of benzonitrile calculated by using the optimized structure with different methods and basis sets. The first line contains the experimental value [7]. In the last line the dipole moment calculated with MP2/6-31G* using the HF/6-31G* optimized geometry is shown.

Method	Basis set	Dipole moment/D
(Exp.		4.3)
HF	STO-3G	3.64
HF	3-21G	4.54
HF	6-31G*	4.84
HF	6-31 + G*	4.93
HF	6-311G**	4.83
MP2	6-31G*	4.42
MP2	6-31 + G*	4.57
(MP2	6-31G*	4.40)

with extended conjugation, to obtain reasonable (not incidental as in the case of HF/3-21G) agreement between the experimental and calculated dipole moments, it is more important to include electron correlations than to use larger basis sets.

Keeping in mind that benzonitrile is a constituent fragment of hundreds of mesogens, and that similar phenomena would probably be observed in biphenyls and heteroatomic conjugated systems, this conclusion seems to be rather general for mesogens: to reproduce the molecular dipole moment with a precision better than 20% one has to include electron correlations (for example at the MP2 level). But for most mesogen

molecules, optimization of the molecular geometry on such a level is not affordable with contemporary computer power. Therefore, keeping in mind the insensitivity of the dipole moments to reasonable variations of the molecular geometry, we checked the possibility of performing HF geometry optimization and subsequently calculating the dipole moment with MP2 afterwards. *A priori* one cannot expect that this will give reasonable results, and for some systems [16], in fact, it does not. But in the present case, sufficiently small variations of the molecular geometry in different approximations (as illustrated in table 3) and the insensitivity of the dipole moment (figure 4) suggest that the method of geometry optimization is not essential. As is seen from the last line of table 4, the differences between the results obtained for geometries optimized with different methods are negligible. Hence for such molecules as benzonitrile (and as we shall see further for its mesogenic derivatives as well) it is possible to calculate the geometry with more simple (and less time consuming) methods. If the electron distribution is calculated on the MP2 level, both HF and MP2 geometries reproduce well the molecular electric properties (even the partial charge distributions calculated for these two differently optimized structures are very similar, as is seen from figure 5).

3.2. *Mesogen prototypes*

Similar conclusions can be drawn for more complex molecules, i.e. for mesogens or molecules that are similar to mesogens. Only in cases when the polar fragments are not directly connected to the conjugated core are the computational requirements not so high. From table 1, one can see that experimental dipole moment values of weakly polar molecules like *p*-methyl substituted biphenyl and phenylcyclohexyl derivatives can be obtained simply on the HF level. With the methods described above, we studied the charge distribution of more polar molecules belonging to the homologous sets *n*-alkyl-*X*-CN, where *X* was bicyclohexyl (*n*CCH), bicyclo-octylphenyl (*n*BCO), phenylcyclohexyl (*n*PCH), biphenyl (*n*CB) and oxybiphenyl (*n*OCB). The alkyl chains have variable length *n*. Molecules with *n* = 1 (1BCO) or *n* = 3 (others) are shown in figure 1. The resulting dipole moments are presented in table 5. The conclusions obtained for benzonitrile are confirmed by the computations of these mesogens: geometry optimization on the HF level and the subsequent electron structure calculations on the MP2 level result in dipole moment values that are almost indistinguishable from the computations made completely on the MP2 level. Therefore we feel this approach to be sufficient for electron structure studies of cyano compounds. Although the resulting dipole moments are not in perfect agreement with experimental data, the deviations do not exceed 15%.
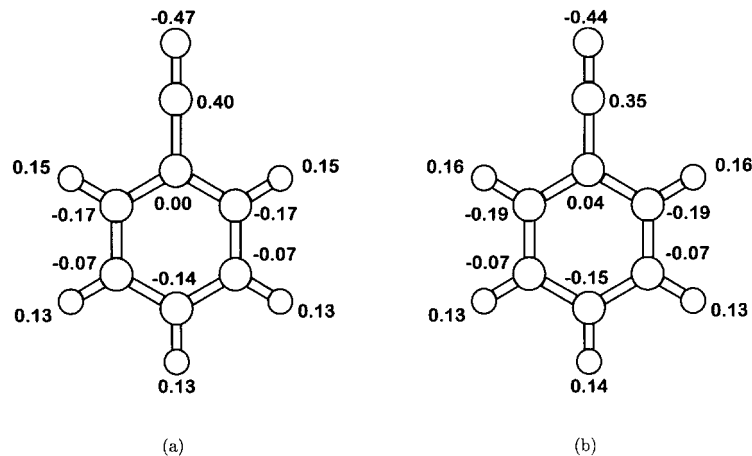
Figure 5. Partial charges of benzo-nitrile calculated with two different models. In (*a*) the Coulomb potential is fitted to the MP2/6-31G*//HF/6-31G* ESP; in (*b*) MP2/6-31G*//MP2/6-31G* ESP was used. The calculated dipole moments of these models are in table 4.

(a)   (b)

Table 5. Dipole moments of several mesogens with different alkyl chain lengths calculated with different models (method for dipole moment computation//method of geometry optimization). All calculations were done with the 6-31G* basis set. Available experimental data are given in the last column. All values are given in Debye.

Substance	Model			
	HF//HF	MP2//HF	MP2//MP2	Exp.
1OCB	5.50	5.00	—	—
2OCB	5.64	5.16	—	—
3OCB	5.74	5.27	—	—
4OCB	5.79	5.32	—	—
5OCB	5.86	—	—	—
0CB	5.45	4.91	4.97	4.51 [17]
1CB	5.90	5.35	5.42	4.94 [17]
2CB	5.88	5.34	5.39	5.01 [17]
3CB	5.90	5.37	—	4.93 [17]
4CB	5.97	5.44	—	5.00 [17]
5CB	5.98	5.43	—	4.77 [18]–4.92 [17]
0PCH	5.66	5.14	5.17	—
1PCH	5.63	5.12	5.16	—
2PCH	5.70	5.19	—	—
3PCH	5.69	5.19	—	4.98 [19]
4PCH	5.73	5.23	—	—
5PCH	5.72	—	—	4.14 [18]–4.27 [19]
0CCH	4.77	4.42	4.43	—
1CCH	4.72	4.39	—	—
2CCH	4.78	4.44	—	—
3CCH	4.74	4.41	—	—
4CCH	4.79	—	—	—
5CCH	4.76	—	—	3.60 [18]–3.83 [20]
1BCO	5.77	5.26	—	—
2BCO	5.85	—	—	—
3BCO	5.84	—	—	—
5BCO	5.87	—	—	4.08 [18]

It is clearly seen from table 5 that the computed dipole moments in all cases are larger than the experimental values. The much better agreement of the results for benzonitrile indicates that incomplete account taken of conjugation effects in the benzonitrile fragment cannot be the reason for this. On the other hand, experiments suggest that the alkyl chain plays a minor role in the formation of the charge distribution (see last column of table 5). To check this, we compare the results for molecules with different hard cores and for increasing lengths of the alkyl chain. As seen from table 5 and figure 6, increasing the alkyl chain length has different
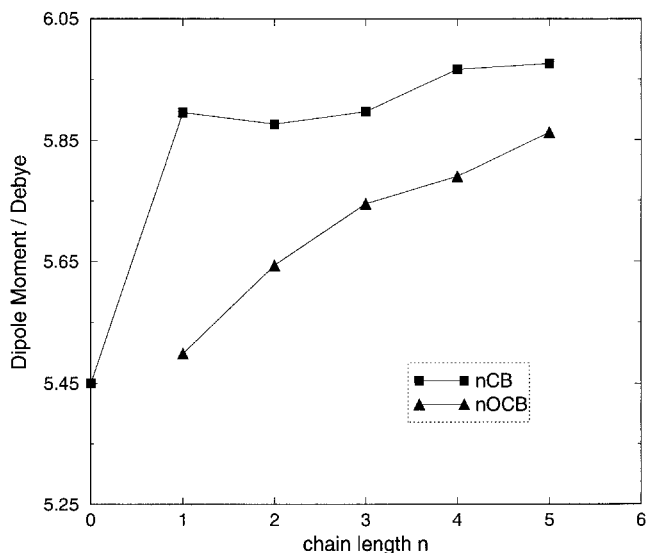
Figure 6. Dipole moments of the homologous *n*CB and
*n*OCB series calculated with HF/6-31G*//HF/6-31G*.
n is the carbon number of the alkyl chain.

effects depending on the molecular core. The increase of
the dipole moment is maximal in those cases where the
alkyl chain is connected to the benzene ring, i.e. for the
*n*OCB and *n*CB sets (the presence of oxygen does not
diminish the effect). This coincides qualitatively and
quantitatively with the conclusions of other groups [21]
where completely different methods were used. Some
experimental data (for example for biphenyl compounds,
as given in table 5) also confirm this conclusion. For
molecules where the alkyl chain is not connected to the
benzene ring, this effect is negligible. Summarizing, the
relation between the computed dipole moments of homo-
logous sets of mesogens is rather reasonable, although
the absolute values might be overestimated.

The experimental values may also be discussed. One
can see that the experimental dipole moment for 5PCH
is similar or even lower than that for benzonitrile. This is
rather unlikely, keeping in mind that there must be some
additional contribution due to polarization effects of the
rest of the molecule. Therefore, although in general the
relative magnitudes of the experimental dipole moments
for the molecules under study are quite reasonable, we
are in doubt about the absolute values. All experimental
measurements for mesogens were performed in the con-
densed phase (in dilute solution) and the local field effect
has been taken into account. These local field corrections
(although subject to discussion [22]), were developed
for compact molecules. For mesogens, the Onsager
cavities are not spherical and it is not clear how to deter-
mine their anisometry. In fact this can result in dipole
moment errors of about 10–20% [22]. Even for com-
pact molecules the experimental dipole moments vary

over a wide range depending on the method used. For
benzonitrile one can find values from 3.77 D [23] to
4.3 D [24].

4. Molecular charge distribution

Quantum chemical computations offer the possibility
to take a detailed look at the electronic structure of the
molecules. This can be done, for example, by determining
atom-based partial charges. Because partial charges are
not quantum mechanical observables, different methods
for deriving them can be chosen. We concentrate on
methods based on fitting the electrostatic point charge
potential to the quantum chemically derived potential.
As seen in figure 3, the results differ quantitatively and
qualitatively depending on the method applied. This has
to be taken into consideration for any discussion of the
charges. Even when the magnitude of the partial charge
is restrained, it varies very much from atom to atom.
In figure 7 we compare the partial charges derived by
applying charge restraints and symmetry constraints to
molecules with different cores. These charges represent
the electrostatic molecular interactions very well, but
they do not show the real charge distribution in the
molecule. Due to the shielding of the carbon charges
by the adjacent hydrogens, the correct electrostatic
potential might be reproduced by different partial charge
distributions. Also, the strong alternation of the charges
of atoms 14 and 15 results in just a small variation of
the electrostatic potential around the molecule. In spite
of these uncertainties, the full set of partial charges is
very useful for molecular dynamics simulations, because
they reproduce the electrostatic potential very well.

Based on the results of our previous simulation studies
of mesogens, where we found a pronounced tendency
for antiparallel pair formation and a decisive influence
of the ESP on the nematic phase stability [25], a
qualitative relation between the ESP of the molecules
and the macroscopic properties of the mesophase can
be found even without extensive molecular dynamics
simulations. As seen in figure 2 (for all details of the
electrostatic potential discussed below we refer to this
figure), the main contribution to the molecular dipole
moment of 3CCH arises from the cyano group and one
can expect strong coupling between the cyano frag-
ments of different molecules in the CCH series. This
effectively elongates the units which are aligned by the
nematic field and increases the transition temperature
from the nematic to the isotropic phase. In view of the
relatively small dipole moment the experimentally obtained
transition temperature for 5CCH in fact is rather high
(see table 6). In comparison with 5CCH, molecules of
the *n*PCH series have substantial positive potential in
the centres of the molecule and one can expect that the
cyano fragments (possessing negative net charge) of

Figure 7. Partial charges of the heavy atoms of molecules with different cores. The charges are calculated as for those in figure 3 using charge restraints and symmetry constraints. The numbers belong to the models shown in figure 3(*a*) (5CB, 5CCH, 5PCH). The numbering scheme for the nitrogen and carbon atoms for 5OCB is the same as in figure 3(*a*). The oxygen on position 20 is located between the aromatic ring and the pentyl chain.
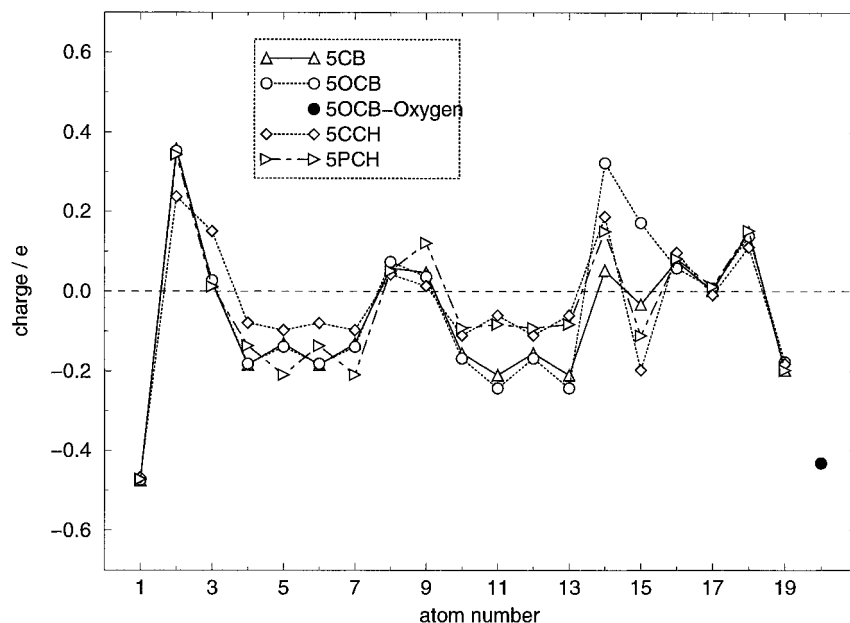
Table 6. Phase transition temperatures for pentyl derivatives with various core structures from [26]. The temperatures for the transitions from crystalline to nematic and from nematic to isotropic phases are given in K. Note that for 5CCH there are transitions to smectic and smectic A phases by cooling from the nematic state.

Substance	Transition temperatures/K
5CB	Cr 296 N 308 I
5PCH	Cr 303 N 328 I
5CCH	Cr 335 (S 312 SmA 323) N 353 I
5BCO	Cr 335 N 373 I
5OCB	Cr 326 N 341 I

the neighbouring molecules will be strongly attracted by it (the formation of antiparallel pairs due to electrostatic interactions was observed in previous molecular dynamics simulations [25]). The overlapping of the molecules, forming antiparallel pairs which could be treated as a single nematic unit, increases in comparison with the CCH series, thus decreasing the transition temperature, although the dipole moment increases (as observed experimentally). For bicyclo-octylphenyl (BCO) a similar ESP is obtained as for PCH. Consequently, the effect of the increased dipole moment compared with PCH becomes essential (experimentally an increase in transition temperature is observed). If we now look at the CB series we see that the positive charge is further shifted to the alkyl tail. This will lead to even higher overlapping of the molecules forming a shorter nematic unit than in the case of PCH. Consequently, neglecting the increase of the dipole moment and the polarizability anisotropy, the mesophase becomes even more unstable (a well-known

experimental fact), although the molecular shape seems to be perfect for nematic phase formation. This is not the case of the OCB series. The oxygen accumulates a strong negative potential and the overlapping of the molecules can no longer be as large as for 5CB. So one can explain the experimentally observed higher transition temperatures for this series.

5. Conclusions

Based on extensive computations, we analysed the extent of reliability of *ab initio* quantum chemical methods for estimating electrostatic dipole moments of some sets of cyano-containing mesogen molecules. We tried to find the level at which such computations give results comparable to available experimental data. We studied only cyano compounds with different rigid cores and alkyl chains, but extension of our conclusions to other molecular structures is mostly straightforward: the presence of conjugation of the polar fragment leads to the necessity to account for electron correlations. Using the derived partial charges as a starting point, molecular dynamics simulations can provide a detailed insight into the molecular arrangement in mesophases, but even without them, we show some examples of how mesomorphic behaviour can be qualitatively explained based on molecular electrostatic potentials.

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