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A comparative study on the nonlinear optical properties of diphenyl ether and diphenyl sulfide compounds

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Fourteen diphenyl ether and diphenyl sulfide compounds were synthesized and a comparative study on their second-order nonlinear optical properties was carried out. The results showed that these two kinds of compounds all had fairly large molecular first-order nonlinear optical hyperpolarizabilities β, but they have very different second harmonic generation (SHG). The diphenyl sulfide derivatives usually have strong SHG effects while almost all the diphenyl ether compounds have no SHG response, which can be attributed to their crystal structure. We found that the diphenyl sulfide compounds were easy to crystallize in a noncentrosymmetric style but the crystal structure of the diphenyl ether derivative was centrosymmetric, and therefore a zero $\chi^{(2)}$ was produced. The atom O or S was the real origin of the difference in their crystal structures, and therefore of the SHG effect.

1. Introduction

Recently organic nonlinear optical (NLO) materials have been paid much attention, which is a result of their promising potential applications in optical information processing, integrated optics and telecommunications.[1] Organic compounds with large delocalized π-electron systems may exhibit extremely larger nonlinear responses, fast switching times and higher laser damage thresholds compared to the currently studied inorganic materials. In addition, the properties of organic materials may be varied to optimize adjunct properties, *e.g.*, mechanical and thermal stability.

It has been generally understood that the strong macroscopic second-order nonlinearity requires not only a large β value but also a noncentrosymmetric crystal structure. Unfortunately, few molecules with large β values crystallize in a noncentrosymmetric style and so it is important to tailor the crystal structures for the optimization of second-order nonlinear properties through chemical manipulation. The factors influencing the crystal structure are very complicated—even a very small change in the molecule can lead to a very different crystal structure—and so very different properties of the NLO materials will be produced. This is the decisive factor for us in designing effective NLO materials.

4-Aminophenyl 4′-nitrophenyl sulfide (ANDS) has a large delocalized π-electron molecular system and was reported as an organic nonlinear optical material by Abdel-Halim.[2] We also studied the NLO properties and the crystal growth habit of ANDS.[3] ANDS is a representative diphenyl sulfide compound and we investigated some other diphenyl sulfide derivatives in the present work. Most of them also had a fairly strong second-order nonlinear response. Diphenyl ether has a very similar molecular structure to diphenyl sulfide and the only difference between them is the atom (O or S) linking the two benzene rings in the molecules. We hoped these diphenyl ether compounds with similar molecular structures would also show a strong SHG response and so prepared some of their derivatives, most of which had the same substituents as the diphenyl sulfides. But to our surprise, the results revealed that almost all the diphenyl ether compounds we studied had no obvious SHG effect though their molecular nonlinearities were big. The details will be discussed in the following sections. In order to have an insight into the molecular orientation in the unit cell the crystal structure of 4-aminophenyl 4′-nitrophenyl ether (ANDE) was determined.

2 Experimental and calculation

The diphenyl ether and diphenyl sulfide compounds were synthesized according to the methods in references 4–8 and 9, respectively. The samples were recrystallized from absolute ethanol three times and then were dried for the measurements. The powder SHG intensities were measured by the conventional technique of Kurtz and Perry[10] using a Q-switched pulse Nd : YAG laser. The wavelength was 1064 nm and the particle size was about 76–154 μm.

A crystal structure determination of ANDE was carried out. The crystals of ANDE were obtained from ethyl acetate ($CH_3COOCH_2CH_3$) solution. A yellow crystal of dimensions 0.58 mm × 0.28 mm × 0.28 mm was mounted on a Rigaku AFCTR diffractometer with graphite monochromated Mo-Kα radiation. The data were collected at a temperature of 296 (2) K and a total of 2624 reflections were collected, of which 1937 reflections were observed.

A dipole can be induced in a molecule in an electric field E and can be considered as a perturbation; the perturbing operator is $H' = -er \cdot E$, where r is the general coordinate of the molecule. We calculated the molecular nonlinear optical hyperpolarizabilities β of the synthesized compounds with the CNDO/S-CI quantum chemistry program,[11] in which we used the perturbation theory and the β equation[12] [eqn. (1) and (2)] obtained according to the Born–Oppenheimer approximation. In terms of the calculated results, we have changed the tensor to vector so that the calculated values can be compared with the experimental results. Thus the tensor β_{ijk} is changed to the vector β_{vec} as follows and the calculated results together with the SHG values are listed in Table 1.

$$\beta_{\text{vec}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \qquad (1)$$

$$\beta_i = 1/3 \sum_k (\beta_{ikk} + \beta_{kik} + \beta_{kki}) \quad i, k = x, y, z \qquad (2)$$

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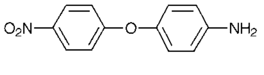
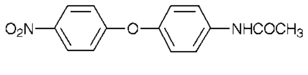
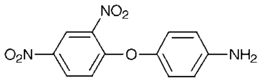
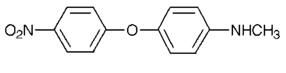
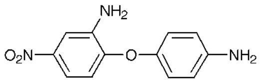
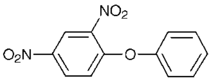
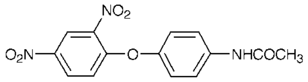
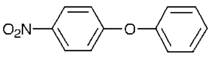
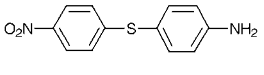
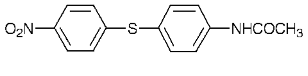
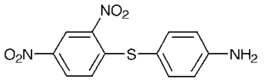
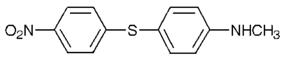
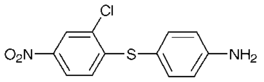
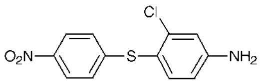
Table 1 The β values and SHG efficiency of the title compounds

Compound	Formula	$\beta/10^{-30}$ esu	SHG/K_2PO_4
1		28.6	0
2		27.6	0
3		21.3	0
4		35.6	0
5		27.0	weak
6		21.2	0
7		33.0	0
8		24.1	0
9		30.4	240
10		29.7	2.4
11		24.5	0
12		39.2	205
13		33.1	5.9
14		28.4	158

3 Results and discussion

From the calculated β values in Table 1 we can see that both diphenyl sulfide and diphenyl ether compounds have fairly big first-order nonlinear optical hyperpolarizabilities; this is the basis of the strong macroscopic nonlinearity. The results of the crystal determination show that the amino-substituted benzene ring of the ANDE molecule is almost perpendicular to the nitro-substituted one. ANDS has a similar molecular structure.[2] Thus the whole molecular conjugation system is disturbed at the O atom and this rules out any contribution to β by charge transfer interaction between the NH_2 and NO_2 substituted moieties of the molecule. Thus the intramolecular charge transfer should be considered as two parts: one is O (S)$\rightarrow NO_2$ and the other is $NH_2 \rightarrow$O (S). The nitro group (NO_2) is a strong acceptor in the molecule and the moiety C_6H_4–O (S) is an excellent donor, so a strong intramolecular charge transfer can be caused when the molecules are placed in an external field E. This is the origin of the strong molecular nonlinearity, as can be proven in the following calculation of ANDE.

Since the intramolecular electron transfer usually occurs from a donor to an acceptor the molecular hyperpolarizability β should be anisotropic. The following are the calculated components of β ($\times 10^{-30}$ esu) of ANDE and Fig. 1 shows its molecular structure and the coordinate system. The ANDE molecule lies in the xy plane and we choose the donor (O)–acceptor (NO_2) as the x axis.

β_{xxx}	β_{yyy}	β_{zzz}	β
-26.8	-2.3	9.7	28.6

The component β_{xxx} contributes about 94% to the β vector, which is mainly from the O$\rightarrow NO_2$ electron transfer. Thus β is one-dimensional to a fairly good approximation. The other part of $NH_2 \rightarrow$O should be the origin of β_{zzz} and β_{yyy}.

The SHG efficiency in Table 1 shows a surprising result. Some of these two kinds of compounds in Table 1 have very similar molecular structures, such as **1** and **9**, **2** and **10**, **4** and **12** *etc*. But most of the diphenyl sulfide compounds have a strong SHG effect except for compound **11**, while almost all the diphenyl ether derivatives have no obvious SHG response. It is obvious that the great difference in the macroscopic nonlinear optical properties of the materials should be attributed to the O and S atoms in the molecules.

Compounds **13** and **14** have the same molecular structure except for the difference in the position of Cl substitution; the 2′-substitution of the Cl radical (compound **14**) is more effective for the macroscopic nonlinearity than the 2-substitution (compound **13**). But the second-order hyperpolarizability of **13** is bigger, which reveals that the main factor leading to the weaker SHG response is the ineffective crystal structure caused by the Cl in the 2-position in the molecule and not the molecular nonlinearity.

From the results we also can see that if one of the benzene rings is substituted with two NO_2 groups at the 2 and 4-positions the SHG response of the materials will vanish. These dinitro-substituted molecular structures must favor centrosymmetric crystal structures and therefore they have no SHG response. Table 2 lists the ground state dipole moments of the studied compounds calculated by a PM3 approximate molecular orbital calculation method. The dinitro-substituted molecules, such as compounds **3** and **11**, have large dipole moments μ. There should be fairly strong dipolar interactions between their molecules in the crystals. Very strong dipolar interactions tend to favor opposing packing of the molecules, which often results in centrosymmetric crystal structures. That is to say, such types of molecular structures as diphenyl ether

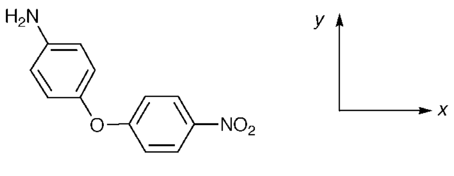


Fig. 1 The molecular structure and the coordinate system of ANDE.

Table 2 The dipole moments of the compounds

Compound	μ/D	Compound	μ/D
1	7.47	**8**	6.16
2	3.90	**9**	7.16
3	8.20	**10**	3.59
4	7.70	**11**	8.82
5	7.78	**12**	7.22
6	7.23	**13**	7.16
7	5.31	**14**	7.10

and diphenyl sulfide derivatives should be avoided in designing NLO materials.

The calculated results of the dipole moments also show that these compounds all have large dipole moments μ except for compounds **2** and **10**, which results from the substitution of the acceptor $COCH_3$ in the opposite position to the NO_2 group in their molecules. If the intermolecular interactions are mainly from the dipole–dipole interactions then the diphenyl ethers and sulfide derivatives should tend to crystallize in a centrosymmetric crystal point group. However, most of the sulfides show strong SHG responses that can prove their crystal structures must be noncentrosymmetric. So we can conclude it is not the dipole–dipole interactions but the other factors which lead to the great difference between the crystal structures of these two kinds of compounds.

As we have discussed above, the diphenyl ether compounds have relatively strong molecular nonlinear optical properties, and so we can conclude that these compounds must crystallize in a centrosymmetric class, which is inactive for macroscopic nonlinearity (SHG effect). To validate this conclusion we determined the crystal structure of ANDE (compound **1** in Table 1). The crystal data for ANDE:† $C_{12}H_{10}N_2O_3$, $M=230.22$, monoclinic, $a=7.234(1)$ Å, $b=8.999(1)$ Å, $c=16.907(2)$ Å, $\beta=92.42(1)°$, $V=1099.6(2)$ Å^3, $T=296(2)$ K, space group $P2_1/c$, $Z=4$, μ(Mo-Kα)$=0.102$ mm^{-1}, 2624 reflections collected, 1937 independent reflections ($R_{\text{int}}=0.0118$). The final $wR_2=0.0770$, $R_1=0.0322$. The absence of SHG response has been proven from the centrosymmetric crystal structure. Besides the molecular similarity of ANDE and ANDS (the two benzene rings are almost perpendicular) their molecular geometry shows some obvious differences: the C(7)–O(1)–C(4) bond angle of ANDE is about 118° while that of ANDS is only about 104°. Such a great difference is certainly caused by the difference between the O and S atoms in their molecules and may be the origin of their different crystal structures. The bond lengths of O(1)–C(4) and O(1)–C(7) in ANDE molecule are 1.3716(16) and 1.4981(16) Å, respectively, but the pertinent bond lengths of ANDS are much longer (1.77 and 1.78 Å).

In order to obtain an idea of the intermolecular interactions an OPEC calculation[13] was carried out on the ANDE crystal structure. The calculation results indicate that the molecules are connected into zigzag chains by an O(1)···H–N(1) hydrogen bond along the *a* axis and these chains are linked across centers of symmetry by fairly strong $\pi\cdots\pi$ interactions between the NO_2 attached benzene rings and O(2)···H–C(5) bond ($-x+1$, $-y$, $-z$), thus forming a two dimensional network. O(3)···H–C(3) (x, $-y-1/2$, $z-1/2$), O(2)···H–N(1) ($-x, y+1/2, -z+1/2$) and O(3)···H–N(1) ($x+1$, $-y-1/2$, $z-1/2$) are the main interactions between layers and form the crystal structure. Fig. 2 and 3 show the packing diagram down the *a* axis and the molecular structure of ANDE showing 50% probability displacement ellipsoids, respectively.

In the ANDS crystal,[2] the hydrogen bonding interactions between one amine hydrogen and one nitro oxygen hold the molecules in a head-to-tail arrangement that is beneficial in forming a noncentrosymmetric crystal structure. Fig. 4 shows the molecular packing in its unit cell. ANDS belongs to the *mm*2 point group and thus has the best crystal structure for the macroscopic second-order nonlinearity according to the conclusion by Zyss and Oudar.[14] The weaker electronegativity of S creates impossibly strong intermolecular interactions and only a weak intramolecular interaction occurs while the O atom in ANDE results in strong intermolecular hydrogen bonding interactions, which benefit from the stronger electronegativity of the O atom and the larger angle at the O atom in the ANDE molecule. Along with the other strong intermolecular interactions this intermolecular interaction leads to an opposite arrangement of the ANDE molecules in the unit cell, and so a centrosymmetric crystal style is formed. That is to say, the atoms O and S play an important role in the crystal structure of these two kinds of compounds and this is the origin of the great difference of the NLO properties of these two kinds of compounds.

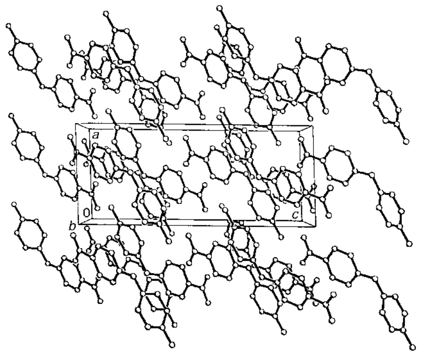


Fig. 2 Packing diagram viewed down the *a* axis.

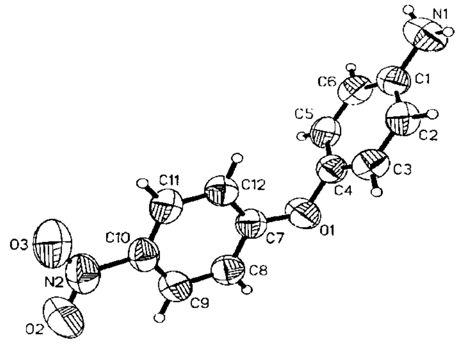


Fig. 3 The molecular structure of ANDE showing 50% probability displacement ellipsoids.

4 Conclusion

The diphenyl ether and diphenyl sulfide compounds have very similar molecular structures and fairly big molecular nonlinear

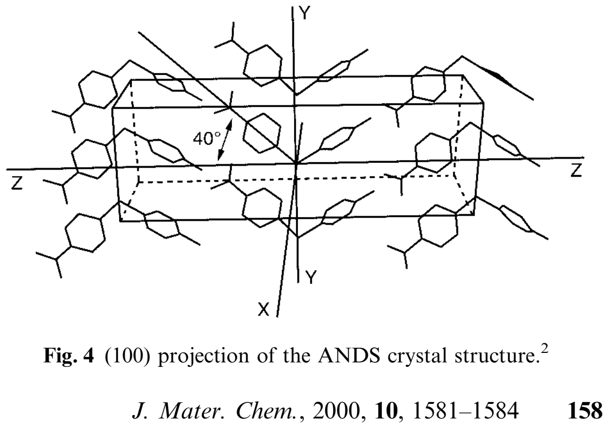


Fig. 4 (100) projection of the ANDS crystal structure.[2]

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†CCDC reference number 1145/219. See http://www.rsc.org/suppdata/jm/b0/b000957l/ for crystallographic files in .cif format.

optical hyperpolarizabilities β. But the diphenyl sulfide derivatives usually have a strong SHG effect while almost all the diphenyl ether compounds have no SHG response, which can be attributed to their different crystal structures. The diphenyl sulfide compounds were easy to crystallize in a noncentrosymmetric style but the crystal structure of the diphenyl ether derivatives was centrosymmetric, and therefore these kinds of compounds usually have no SHG response. The great difference in their crystal structures can be attributed to the atoms O and S linking the two benzene rings in the molecules.

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