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($x = 0.50$), 138855-75-1; $La_{1-x}Sr_xTiO_3$ ($x = 0.60$), 120501-49-7; $La_{1-x}Sr_xTiO_3$ ($x = 0.70$), 120501-50-0; $La_{1-x}Sr_xTiO_3$ ($x = 0.80$), 120501-51-1; $La_{1-x}Sr_xTiO_3$ ($x = 0.90$), 120501-52-2; $La_{1-x}Sr_xTiO_3$ ($x = 1.00$), 12060-59-2; $La_{1-x}Sr_xTiO_3$ ($x = 0.00$–1.00), 138855-76-2.

Supplementary Material Available: Figures of observed, calculated, and difference profiles obtained from the neutron powder diffraction data (4 pages). Ordering information is given on any current masthead page.

Straight-Chain Carbamyl Compounds for Second Harmonic Generation

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Straight-chain alkyl and analogous polymethylene esters and amides of nitrophenyl carbamic acids (urethanes and ureas) have been found to yield acentric crystals having nonlinear optical properties. These crystals displayed powder second harmonic generation efficiencies ranging from 0 to 154 times that of urea, depending on the crystallizing solvent and the crystallizing conditions employed. Powder X-ray diffraction *D* spacings were employed to characterize the exact crystal form of each sample of material studied.

Introduction

The possibility of using organic compounds in nonlinear optical (NLO) devices has generated much interest recently because numerous types of molecules are available for investigation. Some substituted aromatic compounds are known to exhibit large optical nonlinearities, and these are enhanced if the molecule has both donor and acceptor groups bonded at opposite ends of the conjugated system.[1] The potential utility for very-high-frequency applications of organic materials having large second-order (and third-order) nonlinearities is greater than that for conventional inorganic electrooptic materials because of the higher dielectric constants of the latter. Furthermore, the properties of organic materials can often be varied to optimize mechanical and thermooxidative stability as well as laser damage threshold.

For a material to be useful in second harmonic generation (SHG), the active NLO moiety must exist in a macroscopically acentric environment. To fulfill this criterion, molecular structures intended for NLO applications frequently include a chiral moiety. It is true that this does not ensure that the NLO-active moiety will be properly oriented in the acentric environment to produce high SHG; nevertheless, as is clearly demonstrated by chiral carbamic acid derivatives,[2] this technique is a reliable one for making molecules which form acentric SHG-active crystals. It is also possible to introduce macroscopic acentricity in a material by the use of an electric field either for poling an amorphous material[3] or for biasing the molecules to crystallize in a desired acentric form.[4]

This report describes a series of acentric achiral compounds which may be regarded as providing a novel route for inducing acentricity in crystals. These straight-chain carbamyl compounds, some of which may also be considered for Langmuir–Blodgett film formation, are characterized by powder X-ray diffraction (XRD) *D* spacings in the exact crystal forms studied for SHG activity.

Experimental Section

The urethanes and ureas were all synthesized from 4-nitrophenyl isocyanate by similar methods; therefore, representative syntheses are shown. The 4-nitrophenyl isocyanate was purified by dissolving it in dry hot toluene followed by filtering to remove all undissolved solids. The principal impurity, bis(4-nitrophenyl)urea, mp 324 °C (dec), is extremely insoluble in most solvents. The filtrate can either be evaporatively cooled to effect crystallization of the 4-nitrophenyl isocyanate or be used as is. Most of the urethanes have been previously reported,[5] but we find slightly higher melting points in most cases. Melting points were obtained on a modified Buchi–Tottoli apparatus, metal-calibrated to the International Temperature Scale of 1990.[6] Differential scanning calorimetry was performed under nitrogen (Du Pont 2100 DSC apparatus; nonsealed sample containers) and verified, by absence of anomalous endotherms, that the SHG samples were not solvates, and the melting points generally agreed with the capillary determination within ±1 °C.

Infrared spectroscopy was used to verify the presence of urethane and urea groups, and proton NMR with integration was used to confirm the structure of each compound.

Synthesis of 1-(11-bromoundecyl)-4-nitrophenyl carbamate: Freshly purified 4-nitrophenyl isocyanate (Aldrich, 9.0 g, 0.055 mol) was dissolved in 100 mL of dry ether in a 250-mL round-bottom flask. To this were added 13.8 g (0.055 mol) of 11-bromo-1-undecanol (Aldrich) and 3 drops of dibutyltin dilaurate in 120 mL of ether. After the exotherm had subsided, the reaction was refluxed for about 2 h before the yellow precipitate was recovered by filtration. Recrystallization from ethanol gave extremely pale yellow crystals in excellent yield (>95%), mp 122–123 °C.

Synthesis of *N*-octadecyl-*N'*-4-nitrophenyl urea: *n*-Octadecylamine (Aldrich, 1.35 g, 0.005 mol) and freshly purified 4-nitrophenyl isocyanate (Eastman, 0.83 g, 0.005 mol) were dissolved in 25 mL of toluene in a 50-mL Erlenmeyer flask fitted with air condenser and heated for about 2 h on a steam bath. The yellowish precipitate which formed on cooling was filtered off and recrystallized from acetone to yield 1.59 g of whitish solid (76%), mp 121–122 °C.

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Table I. Crystallization and Powder Second Harmonic Generation Data for Straight-Chain Urethanes of Structure $4\text{-}NO_2C_6H_4NHCOOR$

no.	R	crystallization solvt	mp, °C found	mp, °C lit.	SHG efficiency
1	CH_3–	MeOH	178–179	180	0.001
2	C_2H_5–	EtOH (hot)	127–128	129	23
2A	C_2H_5–	EtOH (cool)	130	129	5.5
2B	C_2H_5–	acetone/MeOH (slow evap)	114–115; then 128–129	129	(0.000)[a]
3	*n*-C_3H_7–	*n*-PrOH	116–117	116	0.000
4	*n*-C_4H_9–	*n*-BuOH	96	95.5	85
5	*n*-C_5H_{11}–	EtOH (hot aq)	93	86	46
5A	*n*-C_5H_{11}–	EtOH (cool aq)	93	86	0.03
6	*n*-C_6H_{13}–	EtOH	104	103	154; high[b]
7	*n*-C_7H_{15}–[c]	EtOH	103–104	102	110
7A	*n*-C_7H_{15}–[c]	EtOH	103–104	102	0.007
7B	*n*-C_7H_{15}–	*n*-BuAc	104–105	102	0.4
7C	*n*-C_7H_{15}–	EtOH	102–103	102	0.4
7D	*n*-C_7H_{15}–	EtOH (hot)	104	102	high[d]
8	*n*-C_8H_{17}–	EtOH	110–110.5	111	62
9	*n*-C_9H_{19}–	EtOH (hot)	108	106	80
9A	*n*-C_9H_{19}–	EtOH	106.5–107	106	13
10	*n*-$C_{10}H_{21}$–	EtOH	112–114	117	99
11	*n*-$C_{11}H_{23}$–	EtOH	113	99.5	20
12	*n*-$C_{12}H_{25}$–	EtOH	116–118	117	8
13	*n*-$C_{13}H_{27}$–	heptane	115		7.6
13A	*n*-$C_{13}H_{27}$–	EtOH	115.5–116.5		7.1
14	$CH_2{=}CH(CH_2)_9$–	EtOH	102.5–103		0.8
15	$HC{\equiv}C(CH_2)_9$–	EtOH	113–114		32
16	*n*-$C_{16}H_{33}$–	EtOH	120	118	2.9
16A	*n*-$C_{16}H_{33}$–	EtOH	120–121	118	60
17	$C_6H_5(CH_2)_5$–	EtOH	74		9
18	*n*-$C_{18}H_{37}$–	CH_2Cl_2	121.5–122	115	14
19	*n*-$C_{19}H_{39}$–	EtOH	119–120		0.5
20	*cis*-*n*-$C_8H_{17}CH{=}CH(CH_2)_8$–	EtOH	88–93		0.5
21	*cis*-*n*-$C_8H_{17}CH{=}CH(CH_2)_{12}$–	isooctane	80		3.6
22	*n*-$C_{22}H_{45}$–	EtOH	123–124		0.6
23	$Cl(CH_2)_6$–	n-PrOH	88–89		24
23A	$Cl(CH_2)_6$–	EtOH	89		18
24	$Br(CH_2)_{11}$–	EtOH	122–123		67
24A	$Br(CH_2)_{11}$–	acetone	123		37
25	$Br(CH_2)_{12}$–	EtOH	101–102		44
26	$Br(CH_2)_{16}$–	EtOH	110–111		23
27	$I(CH_2)_{11}$–	EtOH	127–129		17
28	$HO(CH_2)_8$–	EtOH (aq)	115–116		10
29	$CH_3S(CH_2)_2$–	EtOH (aq)	75		18

[a] Not measurable due to insufficient sample; required by centrosymmetric structure established by single-crystal X-ray analysis. [b] Observed visually as a bright green powder luminosity when irradiated by a Nd:YAG laser emitting at 1.064-μm wavelength. [c] These samples resulted from separate crystallizations from ethanol. The obvious disagreement between the powder X-ray patterns (Table II), signifies discrete crystal structures, which resulted from unobserved subtle differences in the details of crystallization. [d] Observed visually as a bright green laserlike beam proceeding from a very thin leaflike crystal when irradiated by a Nd:YAG laser emitting at 1.064-μm wavelength.

The powder SHG tests were performed as outlined by Kurtz and Perry[7] using recrystallized urea, crushed and sieved (metal mesh) to between 80 and 180 μm and index-matched by a nonvolatile fluid of refractive index 1.57 (Cargille Scientific Co.), as the standard. Reagent-grade urea is typically "prilled" and microcrystalline and thus shows only about one-fifth of its true signal, an error which, if unrecognized, would result in reporting measurements too high by a factor of 5. Urea was recrystallized (e.g., from water) not to purify it but to grow crystals larger than the test size; these were crushed and sieved in the same manner as the samples for test. The SHG efficiencies for the compounds synthesized, crushed (not ground; grinding of pigments is well-known to cause crystal structure transformations), and sieved as above and index-matched by a nonvolatile fluid of refractive index 1.63 (Cargille Scientific Co.) are listed in Tables I and III along with the crystallizing solvent and melting points. It is conceded that the longest chain compounds are most poorly index-matched by this choice of fluid. Poor index matching results in a decrease in SHG signal.[7] The sub-80-μm fractions of the same sieved samples were analyzed by means of an Automatic Powder Diffractometer Model No. APD-3600 (copper target, λ = 1.5405 Å, Philips Electronic Instruments, Inc., Mahwah, NJ) to establish their XRD patterns in the exact crystalline state in which the SHG tests were conducted. Characterization data are listed in Tables II and IV; in the interest of brevity, only the *D* spacings of the 16 strongest lines and their relative intensities are recorded.

Single-crystal X-ray structure determination was carried out using an Enraf-Nonius CAD 4 diffractometer using Mo Kα radiation and a graphite monochromator. Data reduction was performed with a PDP-11/44 computer using SPD-PLUS (Enraf-Nonius/ B.A. Freng & Assoc.); hydrogen atoms were located and positions refined by least-squares.

Results and Discussion

Chiral group attachment has been used to induce acentricity in carbamic acid derivatives, as shown by Tiers.[2] Cocrystallization, taking advantage of the directionality of hydrogen bonding, may in certain cases induce acentricity.[8,9] In the present work the possibility of straight-chain (polymethylene) "tails" interacting and

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Table II. Powder X-ray *D* Spacings and Intensities for Straight-Chain Urethanes of Table I

no.	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*
1	8.32	3.0	8.23	2.8	7.10	3.1	6.40	11	4.66	10	4.09	2.5	3.57	5	3.482	1.2
2	16.68	100	8.21	34	6.29	6	5.82	21	4.88	61	4.01	49	3.83	13	3.68	16
2A	16.03	100	8.10	39	6.21	8	5.77	27	4.84	72	3.98	59	3.80	10	3.66	13
2B[a]	9.78	13	9.29	15	7.47	76	7.19	5	6.94	30	5.43	7	5.05	58	4.65	11
3	9.96	2.5	5.32	1.4	4.92	1.7	4.53	2.2	4.11	4.6	3.73	4.3	3.66	2.2	3.59	2.4
4	18.00	100	9.06	38	5.34	32	4.74	90	4.46	18	4.22	10	4.08	26	3.94	9
5	21.61	100	10.82	10	5.38	3	5.22	4	4.91	7	4.29	4	4.02	2	3.83	6
5A	22.00	100	10.86	13	5.33	4	5.06	6	4.90	3.4	4.23	3.5	4.01	6	3.87	7
6	20.91	100	10.69	29	5.35	15	5.24	18	4.71	50	4.25	6	4.13	23	3.90	12
7	24.72	100	12.22	4	6.05	3	5.29	7	4.79	28	4.26	5	4.12	5	3.99	6
7A	23.77	100	5.14	12	4.99	12	4.87	9	4.74	19	4.22	12	3.98	11	3.86	18
7B	23.66	100	11.94	12	5.98	10	5.10	8	4.99	8	4.86	6	4.73	13	4.21	10
7C	24.32	100	12.15	14	5.12	18	5.00	19	4.74	26	4.22	14	3.98	15	3.85	18
7D	23.90	100	11.84	5	5.96	4	4.75	2.3	4.22	1.1	3.97	7	3.86	1.7	3.72	1.4
8	24.38	100	12.44	2.4	8.27	1.5	6.17	5	5.21	7	4.73	20	4.21	10	4.09	11
9	26.57	95	6.75	28	5.19	20	4.76	100	4.47	19	4.29	24	3.89	41	3.82	33
9A	27.69	33	6.73	29	5.17	21	4.75	100	4.45	21	4.28	26	3.88	45	3.81	40
10	27.74	100	6.94	24	5.15	6	4.71	19	4.60	21	4.25	10	3.94	14	3.57	21
11	30.05	100	7.56	32	5.15	8	5.02	10	4.77	36	4.34	11	4.28	6	4.11	6
12	30.50	100	7.64	24	5.16	8	5.07	7	4.77	25	4.34	9	4.14	3	3.78	30
13	33.54	100	8.39	26	5.57	7	5.10	18	4.75	93	4.36	23	4.15	13	3.95	8
13A	33.01	80	8.33	50	5.55	11	5.09	19	4.74	100	4.36	27	4.14	23	3.94	29
14	30.15	100	7.45	5	5.15	3	4.91	2.5	4.71	4	4.27	2.6	3.88	1.6	3.69	6
15	28.48	60	7.10	24	5.08	32	4.86	53	4.71	34	4.64	34	4.21	22	3.76	55
16	37.47	52	18.60	47	12.47	12	9.41	52	6.27	24	5.04	32	4.70	87	4.36	45
16A	37.67	100	18.81	12	9.45	9	6.28	3	5.06	14	4.72	36	4.37	19	3.87	10
17	26.63	100	5.00	31	4.78	51	4.53	26	4.37	33	4.31	30	4.06	30	3.97	26
18	40.63	75	20.32	35	13.53	14	10.15	21	6.78	15	5.50	4	5.00	43	4.69	100
19	42.99	100	21.35	34	14.33	45	10.80	30	7.18	25	5.37	8	5.00	7	4.72	39
20	40.65	4	20.32	0.9	13.63	2.6	9.98	2.4	6.86	1.9	5.49	1.1	4.94	50	4.70	100
21	49.57	100	24.75	24	16.50	18	12.01	3	8.17	8	7.16	2	6.38	1	5.34	8
22	46.58	40	23.21	26	15.58	18	4.93	47	4.66	94	4.40	52	4.02	9	3.89	16
23	7.80	17	5.13	29	4.82	45	4.51	17	3.95	41	3.88	100	3.79	24	3.59	12
23A	5.14	46	4.83	72	4.53	27	4.22	15	3.97	57	3.89	100	3.82	74	3.69	21
24	15.55	100	10.42	87	4.74	45	4.54	29	4.16	53	3.89	42	3.80	91	3.63	62
25	33.43	5	16.71	100	11.14	31	6.69	7	4.89	4	4.73	22	4.35	9	4.30	10
26	19.30	100	13.06	46	7.91	65	4.91	20	4.84	13	4.67	85	4.36	42	4.24	18
27	16.62	87	16.37	100	10.94	56	8.18	11	6.49	14	4.27	5	4.01	16	3.86	5
28	25.89	100	8.57	8	6.42	1.4	5.14	1.3	5.02	1.4	4.82	3	4.28	4	4.15	1.7
29	19.05	100	9.43	20	5.14	76	4.68	54	3.77	5	3.63	8	3.56	19	3.307	37
1	3.312	8	3.216	100	3.150	3.1	2.626	2.2	2.588	1.9	2.491	1.5	2.200	1.4	2.095	2.2
2	3.54	52	3.331	4	3.175	30	3.141	27	2.661	7	2.491	5	2.460	8	2.185	3.4
2A	3.55	24	3.52	39	3.156	35	3.124	26	2.650	11	2.479	9	2.450	12	2.204	5
2B[a]	4.535	10	4.371	13	3.976	8	3.914	16	3.590	5	3.545	6	3.307	100	3.173	16
3	3.450	100	3.200	1.5	3.150	1.4	2.949	1.3	2.849	1.1	2.777	3.7	2.644	1.3	2.000	1.1
4	3.68	42	3.57	93	3.496	9	3.334	60	3.065	19	2.980	20	2.411	10	2.027	6
5	3.63	6	3.56	5	3.500	5	3.356	10	3.204	1.5	3.058	3	2.432	1.5	2.162	1.1
5A	3.82	5	3.70	2.6	3.63	6	3.51	9	3.425	11	3.345	5	3.282	2.9	3.053	5
6	3.84	6	3.62	16	3.55	26	3.421	41	3.345	16	3.057	9	2.545	5	2.133	6
7	3.91	6	3.73	13	3.66	19	3.498	13	3.413	2.4	3.252	15	2.984	3	2.452	1.2
7A	3.77	12	3.73	13	3.65	17	3.54	21	3.442	23	3.371	15	3.341	20	3.188	14
7B	3.96	19	3.85	14	3.73	10	3.64	15	3.53	20	3.434	17	3.332	19	3.181	12
7C	3.77	14	3.73	19	3.64	20	3.53	21	3.436	26	3.373	13	3.337	18	3.183	16
7D	3.64	3	3.53	3	3.435	2.0	3.394	2.2	3.330	2.5	3.239	1.2	3.181	1.4	2.382	1.1
8	3.78	2.7	3.71	8	3.57	4	3.50	2.3	3.323	12	3.069	3.4	2.459	3.3	1.887	1.3
9	3.64	41	3.51	88	3.422	43	3.347	17	3.197	42	2.977	16	2.242	9	2.081	7
9A	3.64	37	3.51	86	3.431	40	3.351	12	3.203	38	3.170	26	2.981	16	2.241	9
10	3.52	5	3.448	19	3.298	3	3.232	9	3.071	3.1	2.299	7	2.131	4	1.840	5
11	3.76	50	3.60	12	3.420	38	3.201	11	3.127	5	3.002	7	2.500	5	2.143	5
12	3.61	6	3.437	21	3.358	3	3.224	5	3.148	3	3.023	4	2.508	2.0	2.156	2.4
13	3.84	5	3.70	14	3.63	26	3.55	7	3.341	17	3.186	8	2.181	4	2.061	4
13A	3.83	13	3.69	39	3.62	91	3.54	23	3.343	57	3.185	22	3.001	12	2.183	10
14	3.66	5	3.53	1.4	3.436	0.5	3.360	1.2	3.323	1.0	3.214	1.4	3.114	1.0	2.441	0.7
15	3.61	100	3.56	71	3.52	53	3.464	36	3.434	22	3.367	32	3.148	36	3.043	21
16	4.13	13	3.86	38	3.72	50	3.58	100	3.419	13	3.327	29	3.258	18	3.098	22
16A	3.73	11	3.60	27	3.431	4	3.340	7	3.263	4	3.108	5	2.524	3	2.151	3
17	3.84	33	3.75	33	3.68	61	3.54	38	3.429	58	3.308	37	3.195	29	3.078	32
18	4.37	65	4.02	23	3.74	12	3.66	8	3.494	17	3.352	8	2.238	5	2.074	4
19	4.42	14	4.27	18	3.87	26	3.70	8	3.62	54	3.56	16	3.400	21	2.086	10
20	4.31	36	3.60	78	2.804	3.0										
21	4.80	33	4.44	6	4.39	7	4.10	4	3.76	14	3.56	23	3.419	22		
22	3.79	85	3.70	50	3.57	100	3.466	19	3.345	28	3.210	18	3.081	12	2.484	10
23	3.437	30	3.409	9	3.352	13	3.236	37	2.918	17	2.645	9	2.394	8	2.340	20
23A	3.60	40	3.487	80	3.425	23	3.361	36	3.251	83	3.119	21	2.926	15	2.342	20
24	3.61	43	3.52	24	3.475	50	3.333	49	3.194	24	2.595	26	2.355	23	2.227	23
25	4.14	15	3.95	9	3.86	5	3.79	6	3.72	4	3.63	22	3.381	5	3.314	9
26	3.93	66	3.85	27	3.70	85	3.58	19	3.53	14	3.444	27	3.338	18	3.274	26
27	3.278	6	3.199	17	2.908	11	2.667	16	2.460	6	2.282	17	2.132	6	1.880	8
28	3.85	8	3.81	6	3.65	13	3.379	1.5	3.265	3	3.140	1.7	2.328	1.4	2.079	1.7
29	3.244	5	3.113	38	3.081	23	2.689	8	2.410	4	2.378	4	2.333	5	1.864	13

[a] These entries were computed from the single-crystal X-ray data; see text.

Table III. Crystallization and Powder Second Harmonic Generation Data for Straight-Chain Ureas of Structure 4-$NO_2C_6H_4NHCONHR$

no.	R	crystallization solvt	mp,[a] °C	SHG efficiency
30	n-C_5H_{11}–	EtOH	131	0.001
30A	n-C_5H_{11}–	acetone/isooctane	133	0.003
31	n-C_6H_{13}–	n-$C_6H_{13}NH_2$	112	0.9
32	n-$C_{10}H_{21}$–[b]	EtOH	118	38
32A	n-$C_{10}H_{21}$–[b]	EtOH	118	(3)[b]
33	n-$C_{12}H_{25}$–	EtOH	118	8
34	n-$C_{14}H_{29}$–	EtOH	121	11
35	n-$C_{16}H_{33}$–	EtOH	120	6
36	n-$C_{18}H_{37}$–	acetone	122	5
36A	n-$C_{18}H_{37}$–	CH_2Cl_2	123	0.000
36B	n-$C_{18}H_{37}$–	THF	123	0.9
37	*cis*-$C_8H_{17}CH{=}CH$-$(CH_2)_8$–	EtOH	105	1.6

[a] Melted with decomposition. [b] These samples resulted from separate crystallizations from ethanol; any technique variations were unnoticed. Sample 32 contained two seemingly different crystal types, small microcrystalline yellow clumps along with some larger elongated transparent plates; sample 32A was principally composed of these larger plates, with the yellow clumps being a minor component. Their X-ray diffraction patterns, reported in Table IV, are clearly different. Comparison of the full X-ray diffraction pattern further suggests that neither can contaminate the other at a level greater than ca. 10% (estimated), allowing for differences in powder pattern quality. It appears reasonable to attribute most, if not all, of the SHG activity to the microcrystalline clumps.

directing crystallization (perhaps acentrically) is explored. To our knowledge, this structural feature has never previously been shown to result in acentric crystal packing. Though precedents exist among diaryl ureas[8,10] and urea itself, it is remarkable that in the present work nearly all of the urethanes and ureas were obtained in acentric forms.

A particular and unique feature of our work is the specific characterization, by powder XRD D spacings, of the crystal form of each sample of material for which SHG efficiencies are reported. Unlike the melting point, element analysis, and NMR, infrared, or mass spectra, these diffraction pattern D spacings are highly characteristic not only for a particular compound but also for its particular crystal structure. Many organic compounds are known to crystallize in more than one form. In recent NLO papers powder XRD patterns (2θ) plots were displayed pictorially for purposes of distinguishing between crystal forms.[9,10] Unfortunately the small scale of the plots renders them very difficult to use for characterization of the samples.

It should be understood that relative line intensities may vary systematically due to varying degrees of sample orientation (i.e., nonrandomness) on the flat plastic slide which carries the sample into the diffraction apparatus; however, the D spacings will remain essentially unaffected. It is evident that systematic relative intensity changes may somewhat alter the choice of the 16 strongest lines, but such changes are extremely unlikely to prevent recognition of identity between two different samples of a compound having the same crystal structure.

A more serious challenge to such recognition exists as D spacings become longer, especially above 10 Å, since very small systematic errors in diffraction angle become translated into increasingly larger errors in D spacing. It is therefore especially important to recognize the second and higher orders of diffraction, which result in D spacings that are precise integral fractions of the longest ones. Inasmuch as these shorter D spacings may be measured accurately by comparison with those from accepted standard materials, it becomes possible not merely to recognize the aforesaid errors but even to make corrections for them. With appropriate attention being given to making any such indicated corrections, it is a straightforward matter to compare data gathered on separate and dissimilar X-ray diffractometers, and thus for any subsequent workers to identify materials identical to those discussed in this report. Ultimately, one may resort to characterization by single-crystal X-ray structure analysis; since programs exist by means of which the single-crystal data may be converted into an "ideal" powder pattern, a method is provided whereby it will be possible to link our SHG results to future definable crystal structures.

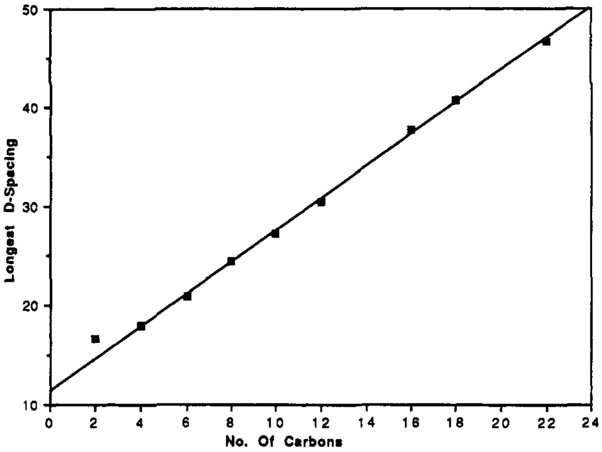

Figure 1. Plot of longest D spacing vs number of alkyl carbon atoms for even-number urethanes.

A plot of the longest D spacing (for paired chains in the crystal) versus the number of carbons in the alkyl chain of the urethanes is shown in Figure 1. A linear relationship is observed. As the alkyl chain increases in length the D spacing increases, by 0.806 (3) Å/CH_2 unit (r^2 = 0.999) for even numbers of carbons and 0.777 (3) Å (r^2 = 0.996) for odd numbers of carbons. (The point for the two-carbon urethane fell significantly off the linear plot, presumably due to differences in its packing due to the relatively short tail.) Comparison of these data with well-known increments (1.275 Å/CH_2) for long-chain hydrocarbons and fatty acids[13,14] indicates the alkyl chains to be inclined at a calculated angle of 50.8° from the normal for even-number carbon chains and 52.4° for chains with odd numbers of carbons. (For this we assumed that the molecules are in a staggered conformation.) From the intercepts (n = 0), 11.39 and 13.56 Å, respectively, it would appear that the 4-nitrophenyl carbamate groups are arranged somewhat differently in the two series. For the ureas, as the alkyl chain increases in length, the D spacing increases by 0.751 (3) Å/CH_2 unit (r^2 = 0.995) for those having an even number of carbons. We calculated a tilt angle of 53.9° in this case, again assuming the molecules are in a staggered conformation. The intercept of 14.14 Å again indicates a somewhat different arrangement of the (4-nitrophenyl)urea and the 4-nitrophenyl carbamate groups.

Even though the usual gradations of melting points are observed as one traverses the homologous series of ure-

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Table IV. Powder X-ray *D* Spacings and Intensities for Straight-Chain Ureas of Table III.

no.	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*	*D*	*I*
30	12.34	8	9.92	8	8.68	12	8.56	12	6.15	14	5.47	16	5.34	8	4.52	11
30A	12.11	22	11.93	14	9.91	14	8.48	38	6.06	31	5.45	47	5.41	31	5.28	25
31	22.92	100	11.26	12	5.53	8	4.77	5	4.58	13	4.21	24	3.92	24	3.74	14
32	29.83	100	7.16	9	4.75	20	4.60	22	4.43	12	4.23	22	4.09	8	3.99	41
32A	28.46	100	9.60	1.0	7.18	10	4.75	4	4.61	1.3	4.44	0.8	4.23	2.5	4.0	6
33	7.95	15	6.11	8	4.78	4	4.65	50	4.49	100	4.20	20	4.01	85	3.82	10
34	34.42	75	17.11	22	8.64	100	5.76	31	4.58	24	4.44	12	4.29	28	4.23	36
35	38.46	100	19.23	8	12.84	4	9.63	10	6.39	5	4.68	3	4.56	5	4.43	4
36	41.54	100	20.66	8	4.69	21	4.64	25	4.45	40	4.23	46	4.08	28	3.95	66
36A	25.02	11	12.55	8	12.35	8	8.25	3	7.04	4	6.21	4	5.09	5	5.03	3
36B	41.26	100	20.63	12	13.77	6	10.34	8	7.47	3	6.85	5	4.62	3	4.52	5
37	40.66	100	20.30	13	13.55	15	10.19	20	6.77	12	4.69	41	4.46	63	4.23	82
30	4.25	27	3.76	31	3.72	100	3.65	8	3.326	9	3.320	11	3.294	8	3.095	7
30A	4.51	22	4.29	21	4.21	20	3.71	100	3.63	19	3.443	17	3.309	25	3.091	22
31	3.65	26	3.496	16	3.406	7	3.352	5	3.228	10	3.081	6	2.951	5	2.092	12
32	3.78	30	3.71	8	3.63	22	3.53	15	3.432	11	3.402	12	3.335	10	3.123	9
32A	3.79	4	3.64	1.3	3.59	1.0	3.53	5	3.408	2.2	3.338	1.0	3.136	1.3	2.823	1.1
33	3.73	13	3.58	15	3.487	25	3.404	2	3.314	7	3.202	2	3.123	10	2.903	2
34	4.04	78	3.88	59	3.83	32	3.60	37	3.50	31	3.436	23	3.307	14	3.271	15
35	4.28	4	4.10	12	4.03	5	3.96	8	3.91	5	3.67	4	3.59	5	3.53	3
36	3.78	22	3.69	44	3.56	30	3.419	11	3.300	10	3.237	8	3.158	8	3.120	7
36A	4.55	30	3.96	3	3.82	100	3.421	34	3.401	51	3.155	6	2.241	3	1.961	3
36B	4.26	7	4.09	13	3.95	14	3.87	6	3.69	5	3.63	6	3.57	6	3.51	3
37	3.91	66	3.77	27	3.66	49	3.52	22	3.397	24	3.247	14	3.169	9	3.111	11

thanes from C_1 to C_{22}, the odd–even trends usually observed in such cases are not very pronounced here. This probably indicates general similarity in crystal packing for these molecules and the leveling effect of the bulky aryl carbamyl unit present in all of them.

Table I indicates a working range for anticipating high SHG efficiencies; alkyl chain lengths between C_4 and C_{11} are very good, and the SHG efficiency falls off after C_{11}, but not to zero. This is attributable in part to dilution by the inactive long chain.

Tables I and III show the dramatic effects of crystallizing solvent on SHG efficiency. The effectiveness of polar solvents in producing acentric, SHG-active, crystal forms has been reported recently.[10,11,15] However, an exactly opposite finding has been made,[12] while in certain cases kinetics of crystallization[16,17] or temperature[18] rather than solvent character were considered to be the determining factor. In other cases[19] no pattern was apparent. The possibility of solvates[17] was ruled out by repetitive DSC as well as by close observation during melting point determinations. For example, the C_7 urethanes, nos. 7–7D in Table I, crystallized from *n*-butyl acetate, ether, and especially the polar solvent ethanol, all showed different SHG values. From this one has to conclude that the orientation of the NLO moiety of the molecule may be solvent-sensitive since the *D* spacings, while not identical, do not suggest radically different chain alignments. The solvent may either encourage the desired parallel packing of the NLO moiety or perhaps facilitate an antiparallel alignment.[11]

For a given solvent, the crystallization temperature can also affect the SHG efficiency of the solid product. For example, when the C_5 urethane (see nos. 5 and 5A, Table I) was crystallized from aqueous ethanol, two sets of crystals were obtained. The first crop was harvested as the hot mixed solvent was cooling, while the other crop of crystals were obtained when the resulting solution, at room temperature, was allowed to evaporate. The first crop of crystals had an efficiency of 46 times that of urea, while the second crop showed an efficiency of 0.03 times that of urea. This factor of 3 powers of ten in SHG efficiency leads one to wonder if the second crop of crystals were actually inactive but contaminated by an otherwise undetected small amount (ca. 0.1%) of the first, which would account for the existence of a small SHG value. Examination by means of a polarizing microscope did detect the presence of crystals apparently resembling the "low-temperature" form in the "high-temperature" sample.

When the ethylurethane was similarly crystallized from ethanol, two sets of crystals were obtained. However, in this case the "high-temperature" crystals, which were fine needles, showed an efficiency of 23 times that of urea while the "low-temperature" crystals, which though tiny were chunky parallelopipeds, showed an efficiency of 5.5 times that of urea. While crystal forms often are an indication of real differences in crystal structure, it is well-known even for sodium chloride that the same internal structure of a material, as shown by powder X-ray spectra, can yield quite differently shaped crystals when one or another facet's growth is retarded by solvent or impurities; and indeed for the two samples of the ethylurethane crystals, nos. 2 and 2A, the powder X-ray *D* spacings and their relative intensities are in sufficiently close agreement as to be judged identical in crystal structure. It is in no way surprising that the SHG efficiencies differ by a factor of about 4, since it is impossible to crush crystal forms so dissimilar in aspect ratio to provide identical sieved powders. Differences in average dimension and/or in aspect ratio may be expected to affect SHG efficiency measurements by perhaps as much as a factor of 5.

The aspect ratio of crystal form 2A was appropriate for X-ray structure analysis, provided that significantly larger crystals could be prepared. This could not be said for any of the other SHG-active materials, and indeed numerous efforts with them were unsuccessful, as were a variety of attempts with the ethyl urethane 2A. Eventually, by slow evaporation of an acetone/methanol solution, a very small batch (2B) of yellow crystals were discovered, from which

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one, of approximate dimensions 0.1 × 0.2 × 0.4 mm was chosen for structure determination. The crystal data for 2B were $C_9H_{10}N_2O_4$, triclinic, $P\bar{1}$ (No. 2), a = 10.697 (5), b = 10.763 (4), c = 9.966 (3) Å, V = 989.3 Å^3, T = 23 °C, Z = 4, D_c = 1.41 g/cm^3, m = 1.1 cm^{-1}, 2731 reflections having $I > 3.00(I)$, R_u = 0.059, R_w = 0.079. The structure of 2B thus was shown to be centrosymmetric and therefore different from the SHG-active 2/2A. Although there was insufficient material for an X-ray powder pattern, the stored single-crystal data for 2B were used to compute an idealized powder pattern, which did not resemble that for 2 or 2A. Later, a small sample of 2B was found to have a metastable melting point (Table I), indicative of it being a different structure. Efforts will continue to produce an XRD-analyzable SHG-active crystal of one of the materials, so that the orientation responsible for activity can be established.

Conclusions

A novel acentric series of crystalline materials has been discovered. Indeed, the attachment of straight-chain polymethylene chains via urethane or urea bridges may be regarded as a new method for inducing crystallographic acentricity. The generality of this method for compounds that are not *N*-(4-nitrophenyl)urethanes or ureas is not known; the lower *N*-alkyl-4-nitroanilines have been studied, but only the butyl derivative had significant SHG activity.[12]

We declare it to be an essential part of the characterization of crystalline NLO compounds to report at least the powder X-ray diffraction *D* spacings of each sample of material so studied. It is our recommendation that this become a requirement for publication of powder SHG efficiency data. Also worthy of consideration as requirements are the specification of sieve size or the like for samples and for standards, and especially due attention to crystal rather than particle size of urea when it is used as a standard.

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Polyphosphazene Molecular Composites. 1. In Situ Polymerization of Tetraethoxysilane

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Composite materials have been prepared by combining polyphosphazene polymers with a silicon oxide precursor, tetraethoxysilane (TEOS), which is polymerized in situ. Poly[bis(methoxyethoxyethoxy)-phosphazene] (MEEP), a polymer that flows at room temperature, forms a clear, flexible, free-standing film when TEOS is polymerized in situ. The storage moduli (E') for the MEEP/TEOS composites exceed 10^9 dyn/cm^2 and the shore A hardness obtained for these materials is ca. 83. In contrast, the corresponding values for the amorphous homopolymer were so low that they could not be measured at room temperature. Preliminary evidence indicates that the etheric side groups of the MEEP are adsorbing to the silicate network and pseudo-cross-linking results. Improved mechanical properties of a (fluoroalkoxy)phosphazene, partially hydrolyzed poly[bis(trifluoroethoxy)phosphazene] (TFEP-OH), were evident in that a rubbery plateau region above (T1) is observed in the storage modulus. The oxide particles are thought to be retarding the movement of the polymer crystallites.

Introduction

In general, polyphosphazenes consist of alternating phosphorus and nitrogen atoms with two substituents per phosphorus.[1,2] Polyphosphazenes have been used as flame retardants, gaskets, fuel lines,[3] and membranes.[4] Recent areas of interest include liquid-crystalline polymers[5] and biological materials.[6] Like polysiloxanes, polyphosphazenes are generally elastomers; the glass transition

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