SPECTROSCOPIC STUDY OF THE STRUCTURE OF o-SUBSTITUTED 2,4-DINITROPHENYLTHIOBENZOATES AND THEIR ALKALINE HYDROLYSIS KINETICS

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Preceding papers have presented results of a study of the kinetics of alkaline hydrolysis of m- and p-substituted 2,4-dinitrophenylthiobenzoates [1] and 2,4-dinitronaphthylthiobenzoates [2]. This paper discusses data on the alkaline hydrolysis kinetics of o-substituted 2,4-dinitrophenylthiobenzoates with the general formula 2,4-$(NO_2)_2C_6H_3SCOC_6H_4$-2'-X, where X = H, CH_3, F, Cl, Br, I, CH_3O, NO_2 (Table 1). We made a parallel study of IR- and UV-absorption spectra of these compounds and of molecules with CH_3 and CH_3O groups in the 4' position, and of some 2,4-dinitronaphthylthiobenzoates and phenylthiofluorobenzoates (2').

IR spectra of thioesters were studied in [3]. It was found that benzene rings, the C=O group, and the S atom form a conjugated system in phenylthiobenzoate molecules. The presence of bulky o-substituents on the C_6H_5 group takes it out of the carbonyl group plane; at the same time, if there is a F atom or OCH_3 group in the o-position, conjugation is preserved but the possibility of conformational isomerism arises [3].

Figure 1 is a model of the 2,4-dinitrophenyl-2'-fluorothiobenzoate molecule (III), which was constructed by taking the van der Waals radii of the atoms into account. Under these conditions, the NO_2 (2) plane, the plane of the benzene ring A, and the SC=O plane are mutually perpendicular. It is also assumed that, other things

TABLE 1. Stretching Vibration Frequencies of the Carbonyl Group in IR Spectra of 2,4-Dinitrophenylthiobenzoates (I)-(IX) and 2,4-Dinitronaphthylthiobenzoates (X)-(XIII)

Compound	Substituent X	ν C=O * cm^{-1} in			
		CCl_4	C_6H_6	CH_3CN	KBr pellets
		2,4-$(NO_2)_2C_6H_3SCOC_6H_4X$			
(I)	H	1692	1691	1690	1683
(II)	2-CH_3	1706	1700	1705	1695
(III)	2-F	1674	1672	1677	1664
		1688 sh	1684	1687	1720
		1712	1713	1716	
(IV)	2-Cl	1707	1675 sh	1675 sh	1699
				1705	
(V)	2-Br	1698	1706	1695	1700
				1725	
(VI)	2-CH_3O	1669	1704	1661	1666
		1711	1662	1707	1700 sh
(VII)	2-NO_2	1710	1709	1698	1650
(VIII)	4-CH_3	1670	1705	1678	1665
		1690	1675	1693	1675
(IX)	4-CH_3O	1665	1695	1672	1668
		1677	1674	1692	1684
		1691	1694		
		2,4-$(NO_2)_2C_{10}H_5SCOC_6H_4X$			
(X)	3-I	1700	1695	1673	1678
		1715 sh		1690 sh	
(XI)	3-NO_2	1685	1685	1685	1685
(XII)	4-CH_3O	1665	1690	1668	1645
		1685		1687	
(XIII)	4-NO_2	1710	1705	1698	1650

* sh denotes a shoulder on the absorption curve.

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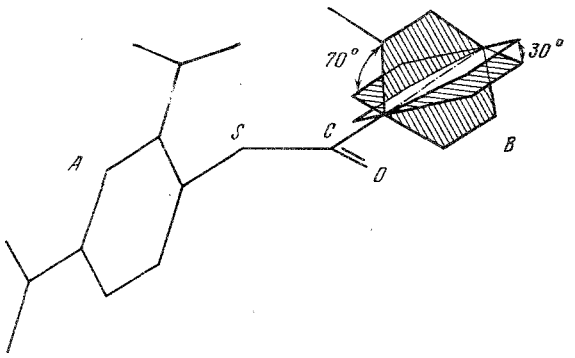


Fig. 1. Three-dimensional model of the 2,4-dinitrophenyl-2-fluorothiobenzoate molecule.

being equal, the molecule's conformation should satisfy maximum overlap of the p(π)-function of the individual fragments. Ring B can occupy four nonequivalent positions. If the F atom is rotated in the direction of the S atom, the dihedral angle between the planes of the benzene ring and SC = O should be ~ 70°; if the F atom is in the cis-position to the C = O group, this angle should not be greater than 140 to 150°. Furthermore, the NO_2 (2) group and the F atom may be found in the same plane as the SC = O group or on different sides of it. Conformations with 70° dihedral angles are apparently less stable and their frequency should increase as the temperature rises.

We took IR spectra in order to study the stereo-structures of these molecules. The most characteristic bands are the stretching vibrations ν(C = O), $\nu_s(NO_2)$, and $\nu_{as}(NO_2)$. The last two appear as broad bands in the 1530 and 1350 cm^{-1} regions. The structure which both of these bands have is probably explained by the fact that the NO_2 groups are not equivalent in positions 2 and 4.

The C = O group appears as one, two, or three absorption bands in the IR spectra of 2,4-dinitrophenyl- and 2,4-dinitronaphthylthiobenzoates in the 1640-1720 cm^{-1} region (see Table 1). The relatively low value of ν(C = O) is due to the low electronegativity of the S atom. The value of ν(C = O) for benzoic acid esters reaches 1750-1760 cm^{-1} and for the phenylthiobenzoate it is equal to 1685 cm^{-1} [4]. Replacement of the benzene ring at the C = O group by a CH_3 group leads to an increase in ν(C = O) to 1711 cm^{-1} [4]. The difference is due primarily to conjugation of the C = O and C_6H_5 groups. The presence of two NO_2 groups on ring A (see Fig. 1) hardly affects the value of ν(C = O). In all probability, this is due to the fact that ring A and the SC = O group are not coplanar, preventing p, π-conjugation between them.

The presence of an o-substituent on ring B is represented in (III), (IV), and (VI) by the complex absorption pattern in the 1660-1720 cm^{-1} region. Similar to what was found in [3] for o-substituted phenylthiobenzoates, we observed a triplet in (III) with absorption peaks at 1674, 1688, and 1712 cm^{-1} (in CCl_4). In the case of (VI), we observed a clearly pronounced doublet (1669 and 1711 cm^{-1}), and for (IV) in benzene and CH_3CN the band with a maximum at 1705 cm^{-1} has a shoulder in the 1675 cm^{-1} region (see Table 1). The presence of such relatively bulky substituents in the 2' position as Br and the CH_3 group is represented by one absorption band ν(C = O) and its maximum is displaced toward the high-frequency region by 10-15 cm^{-1} relative to the analogous line in the spectrum of (I). The position of this maximum corresponds to the frequency of the short-wave component of the doublets of compounds (IV) and (VI) and the triplet of (III). Additional studies of the latter three compounds have shown that increasing the temperature from −60 to +60°C raises the relative "weight" of the band whose maximum is 1710 cm^{-1}. The weight of the high-frequency component also increases when the dielectric constant of the solvent is raised.

It is natural to attribute the bands in the 1660-1690 cm^{-1} region to conformations with a dihedral angle φ ($SCOC_6H_4X$) of 140-150°. The high-frequency band apparently corresponds to "nonplanar" conformations with values of φ close to 90°. It would be logical to assume that the doublet in the 1660-1720 cm^{-1} region in (III) arises from nonequivalent positions of the F atom with respect to the NO_2 (2−) groups. However, the presence of three bands in the spectrum of phenylthiofluorobenzoate (2') (1666, 1690, and 1716 cm^{-1}) contradicts this hypothesis. We must probably agree with the hypothesis that Fermi resonance is present in this case [3]. This reason for the doublet is most probable for compounds (VIII), (IX), (X), and (XII). We should also bear in mind the possibility of intermolecular donor−acceptor interaction between the molecules of the 2,4-dinitrophenylthiobenzoates. However, an attempt to obtain complexes with charge transfer between these molecules and tetracyanoethylene was not successful. A study of IR spectra of (IX) in different concentrations in C_6H_6

TABLE 2. UV Absorption Spectra of 2,4-Dinitrophenylthiobenzoates (I)-(IX) and 2,4-Dinitronaphthylthiobenzoates (X)-(XIV)

Compound	Solvent*	λ_{max}, nm (ε·10⁻³)
(I)	a	207 (20,70), 249 (23,30), 301 (10,70) sh
	d	253 (24,16), 302 (11,83) sh
	wd	256 (21,68), 314 (9,35) sh
(II)	a	206 (43,60), 252 (21,10), 294 (11,90) sh
	d	253 (22,25), 296 (13,33) sh
	wd	254 (15,94), 300 (8,59) sh
(III)	a	205 (22,90), 244 (26,50), 293 (12,50) sh
	d	248 (22,68), 294 (11,16) sh
	wd	251 (22,35), 296 (10,45) sh
(IV)	a	211 (31,60), 244 (24,20), 292 (13,10) sh
	d	249 (18,52), 296 (10,74) sh
	wd	250 (15,51), 298 (8,02) sh
(V)	a	209 (32,80), 246 (19,00), 296 (10,30) s h
	d	249 (18,12), 294 (10,47) sh
	wd	250 (18,03), 296 (9,76) sh
(VI)	a	211 (30,00), 253 (23,20), 314 (13,00)
	d	212 (35,74), 256 (21,29), 318 (12,04)
	wd	212 (34,50), 259 (20,67), 322 (10,93)
(VII)	a	206 (30,00), 220 (27,50) sh, 252 (17,10) sh, 296 (8,70) sh
(VIII)	a	202 (40,60), 215 (24,50) sh, 263 (24,30), 318 (9,50) sh
(IX)	a	200 (34,50), 218 (22,95), 290 (23,50), 333 (10,90) sh
	d	221 (23,62) sh, 288 (22,07), 333 (12,76) sh
	wd	221 (13,30), 291 (12,33), 342 (5,58) sh
(X)	a	228 (47,90), 257 (23,20) sh, 307 (4,80) sh, 357 (1,80) sh
(XI)	a	216 (47,80), 253 (36,40), 370 (6,40)
(XII)	a	206 (52,30), 215 (46,90) sh, 259 (23,10) sh, 288 (29,60), 352 (7,00) sh
(XIII)	a	204 (55,00), 260 (35,70), 351 (7,80) sh
(XIV)	a	200 (46,30), 235 (18,00), 270 (7,00)
	d	236 (18,93), 274 (7,38)
	wd	237 (18,90), 275 (8,38)

* a denotes acetonitrile; d denotes dioxane; wd denotes 50% (dioxane + H_2O); sh denotes a shoulder on the absorption curve; (XIV) is phenylthiofluorobenzoate (2').

revealed that the ν(C = O) absorption band intensities are not concentration dependent. An attempt to detect H-bonds between the C = O group of the compounds studied and phenol molecules through the IR spectra also gave no results. We studied mixtures with phenol to 2,4-dinitrophenylthiobenzoate ratios of 1:10 to 10:1. No displacement of the ν(OH) absorption band was found in the first instance, and in the second case, none in ν(C = O). We think the probable reason for the absence of interaction is the poor stereo access to the C = O group.

We obtained further data on the effect of substituents on the chromophore centers of 2,4-dinitrophenylthiobenzoates by measuring their UV spectra (Table 2). We can assume from the structure of these molecules that the A ring π-electron system substituted by two NO_2 groups is an independent isolated chromophore fragment and the NO_2(2) group is not conjugated with the benzene ring. Consequently, this grouping within the molecule should absorb in the 220-300 nm region in the manner of nitrobenzene (λ_{max} ~ 260-270 nm, ε_{max} ~ 6000-7000). The isolated SC = O groups and the B ring should be represented in the 220-300 nm region by the bands λ^{B}_{max} ~ 260 (ε_{max} ~ 500-1000) and λ^{SCO}_{max} ~ 230-240 nm (ε_{max} ~ 6000) [5]. The spectra of (II) and (V) are characterized by the bands λ^{I}_{max} ~ 295, $\varepsilon_{max}{}^{I}$ ~ $10 \cdot 10^3$ and $\lambda_{max}{}^{II}$ ~ 250 nm, ε^{II}_{max} ~ $20 \cdot 10^3$. The second one of these is absolutely complex and probably corresponds to two electron transitions, one of which is localized on the nitroaromatic part of the molecule, while the second is susceptible to substitution of ring B and is shifted to the low-energy region as the electron-donor properties of the substituent in positions 2 and 4

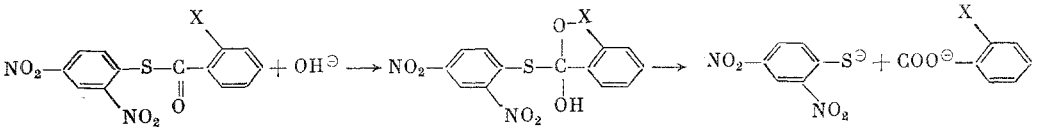
TABLE 3. Alkaline Hydrolysis Reaction Parameters for Compounds (I)-(VII)

Compound	lg K			$\frac{\lg K_0}{\lg K_p}$ (20°)	E_a	$\Delta H^{\neq}$	$\Delta S^{\neq}$, entropy units
	20°	30°	40°		kcal/mole		
(I)	1,497	2,078	2,300	1	22,9±0,1	22,3	−27,0±0,1
(II)	0,947	1,528	1,948	0,57	21,1±0,3	20,5	−15,7
(III)	2,369	2,588	2,905		11,2±0,1	10,7	−11,3
(IV)	1,934	2,217	2,615	0,78	14,4±0,1	13,7	−3,0
(V)	1,802	2,003	2,415	0,72	13,0±0,1	12,4	−8,0
(VI)	0,810	1,143	1,863	0,54	22,0±0,5	21,4	−18,4
(VII)	2,330	2,501	2,830	0,66	10,4±0,1	9,9	−14,2

increase. The band in the 290-300 nm region apparently belongs to a transition involving intramolecular charge transfer from benzene ring B and its ortho- and para-substituents to the C = O group. The retention of this band in (II) and (V) is evidence that the dihedral angle between ring B and the SC = O group does not reach 90°. However, a comparison of the data for compounds (II) and (VIII), for instance, indicates that in the first case the conjugation between the C = O group and the aromatic portion of the molecule is significantly disrupted. The NO_2 groups on ring A have an obvious effect on the position of bands λ^{I} and λ^{II}. Since intermolecular interaction as well as conjugation of ring A with the S atom is not very probable, we can assume that the reason for the effect is a strong intramolecular dipole–dipole interaction that lowers the energy of transitions that are accompanied by transfer of a significant electron charge to the C = O group.

We also obtained spectra of four naphthyl derivatives, (X)-(XIII), and observed the effect of the substituents in ring B on the position of the long-wave electron transitions.

We may therefore expect that the reactivity of the compounds studied depends on the conjugation of the C = O group with the benzene ring, and then the charge transfer should be the result of both the mutual stereo orientation of these groups and the electron-donor and acceptor properties of the substituents. We studied the alkaline hydrolysis reaction that takes place as follows:



This is a second-order reaction. Table 3 shows the results of kinetic measurements and the thermodynamic parameters. The logarithms of the rate constants of the alkaline hydrolysis of o-substituted 2,4-dinitrophenylthiobenzoates are lower than those of the p-derivatives by a factor of 1.5-2.

We calculated a two-parameter correlation between log $K^{25°C}$ and the induction (σ^*) and resonance (σ_R^0) constants. The regression equation follows:

$$\lg K^{20°} = 1{,}30(\pm 0{,}3)+0{,}26(\pm 0{,}09)\sigma^*+1{,}29(\pm 0{,}95)\sigma_R^0$$
$$R = 0{,}85;\ s = 0{,}40$$

The correlation is poor and the relationship with the resonance constant is indefinite. The point for compound (VII) deviates most from a linear relationship; it has an NO_2 group in position 2 and since it is a strong dipole, the effective value of its inductive effect can vary significantly depending on its orientation to the reaction center. We calculated the regression equation without taking the data for this compound into account:

$$\lg K^{20°} = 1{,}36(\pm 0{,}22)+0{,}43(\pm 0{,}10)\sigma^*+2{,}85(\pm 0{,}98)\sigma_R^0$$
$$R = 0{,}93;\ s = 0{,}29$$

The equation's parameters are greatly improved, but on the whole the correlation is still weak, as before. The link with the induction constant is more definite. The point calculated for compound (III) (−0.37) deviates most from the experimental point; this compound had the greatest degree of conformational nonuniformity. Of significant importance for this molecule is apparently the effect of the field induced by the F atom and the change in the character of the intramolecular dipole–dipole interactions.

TABLE 4. Physicochemical Properties of o-Substituted 2,4-Dinitrophenylthiobenzoates (II)-(VII)

Compound	% Yield	mp, °C	Found, %			Empirical formula	Calculated, %		
			C	H	N		C	H	N
(II)	83	93–100	52,79	3,36	8,25	$C_{14}H_{10}N_2O_5S$	52,83	3,14	8,50
(III)	98	99–101	48,62	2,39	8,52	$C_{13}H_7N_3O_5S$	48,44	2,14	8,69
(IV)	96	122–123	46,20	2,15	8,55	$C_{13}H_7N_2O_5S$	46,08	2,06	8,29
(V)	97	127–129	40,87	1,99	7,57	$C_{13}H_7N_2O_3S$	40,73	1,82	7,31
(VI)	81	130–132	50,13	5,08	8,56	$C_{14}H_{10}N_2O_6S$	50,30	2,99	8,38
(VII)	66	–	44,36	1,75	12,41	$C_{13}H_7N_3O_7S$	44,70	2,00	12,03

The regression equation indicates that the alkaline hydrolysis reaction rate rises as constant σ^* and the electron-acceptor properties of the substituent increase. The same conclusion can be reached by operating on the calculated activation energy values for the reaction and the enthalpy change.

We also calculated the functions log K = f(log $K^{20°C}$), which have the form:

$$\lg K^{30°} = 0.66(\pm 0.16) + 0.81(\pm 0.04) \lg K^{20°}$$
$$r = 0.97;\ s = 0.14$$
$$\lg K^{40°} = 1.32(\pm 0.05) + 0.65(\pm 0.02) \lg K^{20°}$$
$$r = 0.99;\ s = 0.05$$

When the temperature is increased, the reaction rate becomes less dependent on the nature of substituent X in o-substituted 2,4-dinitrophenylthiobenzoates. The reverse is true of the p-substituted compounds. In our opinion, this effect is due to an increase in the relative fraction of "nonplanar" conformations as the temperature of the reaction is increased.

EXPERIMENTAL

ortho-Substituted 2,4-Dinitrophenylthiobenzoates. We boiled 1 mole of o-substituted benzoic acid and 2-4 moles of $SOCl_2$ for 3-4 h. The excess $SOCl_2$ was distilled off. The corresponding chloroanhydrides were separated by vacuum fractionation. The separated chloroanhydrides were reacted with KOH in 99% C_2H_5OH at 10-15°C for 1-2 h to obtain the potassium salts of the o-substituted thiobenzoic acid, which were treated with dilute HCl (pH 3-4) to convert them to o-substituted thiobenzoic acids in the form of oily liquids. Treating the acids with alcoholic KOH solution formed their K salts. The o-substituted 2,4-dinitrophenylthiobenzoates were prepared by reacting 1 mole of 2,4-dinitrochlorobenzene with 1.2 mole of the K salt of the o-substituted thiobenzoic acids in 99% C_2H_5OH at ~ 20°C for 1-2 h. Table 4 shows the results of the synthesis of the o-substituted 2,4-dinitrophenylthiobenzoates.

Freshly distilled and carefully purified dioxane was used in all the kinetic measurements. A standard pH 9.22 buffer solution was used. Analytically pure o-substituted 2,4-dinitrophenylthiobenzoates were dissolved in dioxane. The solution concentration was 4 to $5 \cdot 10^{-3}$ mole/liter. The kinetic measurements were made on a Unicam SP-800 spectrophotometer with the working solutions previously thermostated for 1-2 h in covered cuvettes (50% dioxane + buffer solution). The solution concentration was 1 to $5 \cdot 10^{-5}$ mole/liter. The photometry was performed at λ = 320 nm.

The IR spectra of the molecules under study were obtained on a Specord IP-75 spectrophotometer (in KBr pellets, and in solution in CH_3CN, C_6H_6, CCl_4). The UV spectra were measured in CH_3CN (C = 0.002 to 0.004 mole/liter; d = 0.006, 0.0107, and 0.0502 cm), dioxane, and 50% aqueous dioxane (C = 0.003-0.0035 mole/liter; d = 0.0107 cm).

CONCLUSIONS

1. The stereo structure of the o-substituted 2,4-dinitrophenylthiobenzoates depends on the nature of the substituent. Fluorine, chlorine, and methoxy derivatives exist in several nonequivalent conformations.

2. Conjugation between the carbonyl group and the aromatic ring is conserved for all the compounds studied.

3. The alkaline hydrolysis reaction rate rises as the constant σ^* of the substituent increases.

4. The alkaline hydrolysis reaction rate becomes less dependent on the nature of the substituent as the reaction temperature falls.

LITERATURE CITED

1. L. S. Prangova, I. Ya. Kvitko, and L. S. Éfros, Reakts. Sposobn. Org. Soedin., 8, No. 2, 371 (1971).
2. L. S. Prangova and S. I. Stojanov, Monatsh. Chem., 106, 1045 (1975).
3. R. A. Nyquist and W. J. Potts, Spectrochim. Acta, 7, 514 (1959).
4. L. S. Prangova, Dissertation, Leningrad (1970), p. 46.
5. B. Wladislaw, H. Viertler, E. Demant, and Berthold, J. Chem. Soc. B, 565 (1971).

PHOTOCHEMICAL REACTION OF ZINC AND MAGNESIUM PORPHYRINS IN VITREOUS MATRICES CONTAINING DONOR AND ACCEPTOR PARTICLES

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In [1, 2] we carried out a detailed study of the kinetics and mechanism of the low-temperature oxidation–reduction electron-transfer reactions involving metal porphyrins. It was found that when vitreous alcoholic solutions of zinc porphyrins (ZnP) were irradiated in the Soret band in the presence of an electron acceptor, charge separation occurred and ZnP cation-radicals were formed together with the reduced form of the acceptor. Subsequent irradiation of the solutions in the absorption bands of $ZnP^{+\cdot}$ led to the regeneration of the initial porphyrin.

The photoionization of metal porphyrins in the presence of acceptor particles is one of the most important pathways in photosynthesis, but it is not the only pathway involved in the oxidation–reduction reactions of these compounds. It is known that metal porphyrins can also be good electron acceptors [3, 4]. In this connection there is great interest in investigating the photoreactions of metal porphyrins in systems containing efficient electron donors. The study of the mechanism of the photochemical reactions of metal porphyrins in the presence of donor and acceptor species is also of great significance in understanding the processes occurring in natural photosynthetic systems as well as in the designing of artificial systems capable of utilizing solar energy.

The use of actual photosensitizers for the creation of systems which efficiently utilize solar energy is only advisable if the photosensitizer is stable when subjected to a long period of irradiation, i.e., it is capable of repeating the oxidation–reduction cycle many times. The study of the photoreactions of metal porphyrins when they are subjected to a long period of irradiation is therefore of contemporary interest.

In the present work we have studied the photochemical reactions of vitreous solutions of zinc and magnesium porphyrins in the presence of donor and acceptor particles under conditions of long period optical irradiation using ESR and optical spectroscopy.

EXPERIMENTAL

The zinc porphyrins (ZnP): meso-$\alpha,\beta,\gamma,\delta$-tetraphenyl (ZnTPP), etio-I (ZnEtio-I), the dimethyl ester of hemato-IX (ZnHemato-IX DME), and the tetramethyl ester of hemato-IX (ZnHemato-IX TME) were kindly supplied by G. V. Ponomarev. The magnesium meso-tetraphenylporphin (MgTPP) was synthesized using the technique described in [5] and the zinc meso-tetra-($\alpha,\alpha,\alpha,\alpha$-O-pivalamidophenyl)porphin (ZnTpivPP) was prepared in the Colman laboratory (J. P. Colman, MIT, USA).

Alcoholic solutions of the complexes ($C \simeq 10^{-5}$ M) were poured out into thin-walled glass ampuls and frozen into vitreous matrices by loading them into liquid nitrogen. The ampuls were clamped in a fixed position in a Dewar flask with a finger-like side arm, where they remained until the experiments had been terminated. In the experiments concerned with the recording of the optical spectra, quartz ampuls with an ellipsoidal cross-section were used such that the walls of the ampul were practically parallel to one another in the region where the spectrophotometer light beam passed through them. The optical path length was 1-2 mm.

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