BENZIMIDAZOLE DERIVATIVES AS INHIBITORS OF THE OXIDATION OF POLYPROPYLENE AND THE EFFECT OF *p*-HYDROXYDIPHENYLAMINE ON THEIR EFFICIENCY*

A. F. LUKOVNIKOV, B. P. FEDOROV, A. G. VASIL'EVA,
E. A. KRASNYANSKAYA, P. I. LEVIN and YA. L. GOL'DFARB

Institute of Chemical Physics, U.S.S.R. Academy of Sciences
N. D. Zelinskii Institute of Organic Chemistry, U.S.S.R. Academy of Sciences

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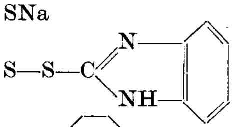
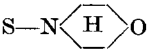
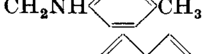
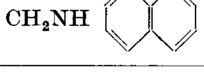
IT IS known [1] that 2-mercaptobenzimidazole and its zinc salt are good inhibitors of the oxidation of rubbers and in some cases phenyl-β-naphthylamine is an efficient antioxidant. It was shown previously by some of us [2] that 2-mercaptobenzimidazole, which is a moderate stabilizer of polyolefins,acquires considerable stabilizing efficiency in admixture with *p*-hydroxydiphenylamine.

However the problem of which of the functional groups (—SH or >NH) of

BENZIMIDAZOLE DERIVATIVES OF STRUCTURE IA AND THEIR RELATIVE EFFICIENCIES AS ANTIOXIDANTS FOR POLYPROPYLENE

Compound	R_1	R_2	M.p., °C	Induction periods, min, for concentrations, mole/kg, of			
				0·02	0·05	0·07	0·1
I	H	SH	303–305†	10–15	150	200	245
II	CH_3	SH	193†	45	85	105	135
III	H	SCH_3	201–202	10	15	15	15
IV	CH_3	SCH_3	58	5	5	5	5
V	H	SNa	—	15	50	65	95
VI	CH_3	SNa	—	15	55	80	110
VII	H		228–230	15	190	270	295
VIII	H		206–209	5	20	35	70
IX	H		175–176	5	25	32	35
X	H		210–220	10	35	50	60

† From alcohol.

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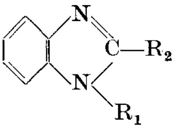
* Vysokomol. soyed. 5: No. 12, 1785–1789, 1963.

mercaptobenzimidazole (MBI) is responsible for the inhibition, or for the increase in efficiency of *p*-hydroxydiphenylamine (HDP) in mixtures, remained unsolved. Meanwhile in order to find the mechanism by which this synergistic system acts it is necessary to know the role of each of the funcional groups of the compound in the inhibition process.

This prompted us to synthesize a number of benzimidazole derivatives (see Table) of the structure:



Ia

in order to examine them as antioxidants for polypropylene and to study their effect in admixture with HDP.

It is seen from the Table that the work was directed toward the substitution of the hydrogen atoms in —SH and >NH groups by mercaptobenzimide radicals. This provided the possibility of following the effect of elimination of labile hydrogen from the functional group.

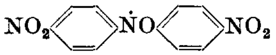
A study was made of the stabilizing effect of each of the tabulated compounds and of mixtures of each with *p*-hydroxydiphenylamine. This study involved the oxidation of polypropylene at 200° and an initial oxygen pressure of 200 mm. The induction period and the dependence of this on the concentration of the compounds were determined. The experimental results for certain concentrations are given in the Table. It is noteworthy that replacement of the hydrogen of the mercapto-group by the CH_3-group (compounds III and IV) causes a sharp reduction in the efficiency of MBI. At the same time substitution of the H-atom of the >NH-group, though it also causes some reduction in efficiency, does not show this effect to the same extent. This indicates that the antioxidant properties of MBI are associated with the SH-group and to a lesser extent with the >NH-group. From which it may also be concluded that in a free-radical chain reaction, as in the oxidation of polypropylene, the mechanism of action of compounds of the type RSH consists in transfer of active hydrogen to the radicals propagating the oxidation chain. It is also quite probable that the RS$^\cdot$ radicals so formed will recombine to form the disulphide or interact with propagating species and terminate the kinetic chain. In these circumstances the following reactions are possible:

$$ROO^{\cdot} + R'SH \rightarrow ROOH + R'S^{\cdot} \qquad (a)$$

$$2R'S^{\cdot} \rightarrow R'SSR' \qquad (b)$$

$$(R^{\cdot})ROO^{\bullet} + R'S \rightarrow \text{chain termination} \qquad (c)$$

Confirmation of the possibility of the occurrence of such processes is provided by the widely known formation of disulphides from mercaptans in oxidation reactions and also by the marked reactivity of mercaptans with stable radicals such as diarylnitrosyl radicals [3], leading to decay of the latter. In the present work we studied the reaction of the 4,4′-dinitrodiphenylnitrosyl radical



with compounds I, III and IV. Compounds III and IV, in which the hydrogen atom of the mercapto group has been substituted proved to be inert toward the stable radical in the temperature range of 20°–50°. On the other hand MBI (I) caused rapid disappearance of these radicals. This reaction was particularly vigorous in the presence of a hydroperoxide (*tert.*-butyl hydroperoxide in our case). The fact that this acceleration of the decay of the stable radicals occurs, can be regarded as an indication of the formation of active radicals (for example $RS^{\cdot}$). It is also evident from the Table that the presence of —S—S— or —SN< bonds in benzimidazole derivatives (see compounds VII and VIII) imparts comparatively high efficiency to the compounds.

2,2′-Dithio-bis-benzimidazole (VII) is particularly efficient. We consider that this is explained by fission of the —S—S— bond with the formation of sulphenyl radicals. This fission is accelerated by increase in temperature and in the presence of free radicals [4]. In this case inhibition of the oxidation process is obviously the result of recombination between the chain-propagating radicals and the sulphenyl radicals (reaction (c)). Compounds of the sulphenamide type (for example VIII) also readily dissociate to form radicals, which again explains their inhibiting efficiency.

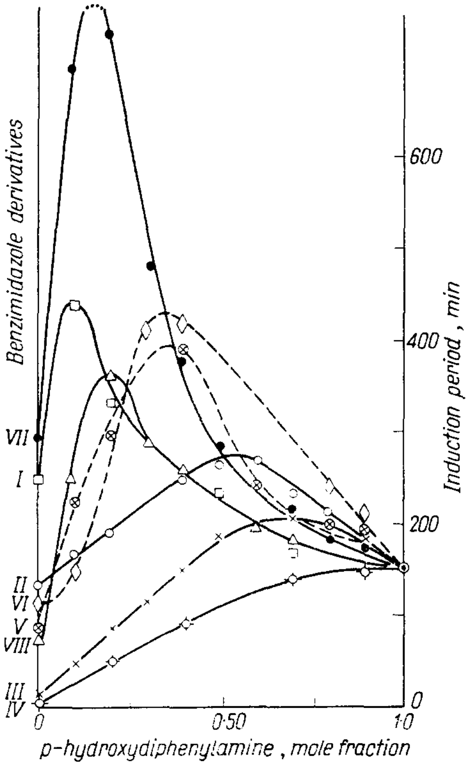
It is interesting to note that sodium mercaptide compounds (V and VI) were also found to be efficient inhibitors. However this question has not yet been studied experimentally.

The introduction into benzimidazole of groups $R_2=CH_2NHR$ (compounds IX and X) has less effect than the introduction of —SH, —S—S— or —SN< groups. It is probable that in this case disturbance of the conjugation of the NH-group with the imidazole ring has an effect.

A similar picture was observed in the study of the stabilizing effect of mixtures of benzimidazole derivatives with HDP. The diagram shows the dependence of the induction period in the oxidation of polypropylene on the molar ratio of HDP to the benzimidazole derivatives in the mixtures. It is clearly seen that 2,2′-dithio-bis-benzimidazole (VII), mercaptobenzimidazole (I) and compounds containing a free —SH or —SNa group (V and VI) or an >SN group (VIII) show a particularly strong synergistic effect. In mixtures of HDP with benzimidazole derivatives containing free NH-groups (III, IX and X) the synergistic effect is either very weak or virtually absent.

The effect of substitution of the H-atoms in the functional groups of MBI is seen very clearly in the case of compound IV, where the curve of the dependence of the induction period on the composition of the mixture coincides with the curve of dependence on the concentration of HDP alone.

Thus in order to obtain high stabilizing efficiency in an individual compound or in a mixture of the compound with HDP it is desirable to introduce into position 2 of benzimidazole a group R_2 = —SH, —S—S—, —S—N< or SMe (K, Na, Zn etc.).



Dependence of the induction period in the oxidation of polypropylene on the molar composition of mixtures of benzimidazole derivatives with *p*-hydroxydiphenylamine. The numbers on the curves refer to the numbers of the benzimidazole derivatives in the Table. Total concentration of mixture 0·1 mole/kg, temperature 200°, initial oxygen pressure 200 mm.

SYNTHESIS OF BENZIMIDAZOLE DERIVATIVES

2-Mercaptobenzimidazole (I) was prepared by the method of Van Allan and Deacon [5] from *o*-phenylenediamine and potassium xanthogenate in ethanol. Yield 90%, m.p. 303–305° (from alcohol).

1-Methyl-2-mercaptobenzimidazole (II) was prepared by heating under reflux for 10 hours a mixture of 30 g of N-methyl-*o*-phenylenediamine, 23·5 g of KOH, 26 g of CS_2, 300 ml of alcohol and 50 ml of water. Yield 26 g (64% of theory), m.p. 193° (from alcohol). According to the literature [10], m.p. 191°.

2-Methylmercaptobenzimidazole (III) was prepared from I (15 g) and methyl iodide (19·8 g) in the presence of 10% NaOH. Yield 73%, m. p. 202–203°. According to the literature [6], m. p. 200°–201° (from dilute alcohol).

1-Methyl-2-methylmercaptobenzimidazole (IV) was prepared by the method of Hunnig and Balli [7] from I, dimethyl sulphate and sodium hydroxide in methanol, in a yield of 70% of theory. The product crystallized after vacuum distillation. m.p. 53° (from alcohol).

Sodium-2-mercaptobenzimidazole (V) was prepared by dissolving I in an equivalent amount of 0·1 N NaOH. The residue after evaporation of the water *in vacuo* was transferred to a filter, washed with alcohol, then ether, and dried *in vacuo* at 100°.

Sodium-1-methyl-2-mercaptobenzimidazole (VI) was prepared by mixing alcoholic solutions of II and an equivalent quantity of sodium alcoholate. The residue after evaporation *in vacuo* was transferred to a filter, washed with alcohol, then ether, and dried *in vacuo* at 100°.

2,2'-Dithio-bis-benzimidazole (VII) was obtained by oxidation of I in alcohol with 27% hydrogen peroxide. This disulphide is insoluble in water and the usual organic solvents.

According to Everett [8] the disulphide has m.p. 198°, but reference [9] gives m.p. 230°. Our compound VII had m.p. 228–230°.

2-(Morpholinomercapto)benzimidazole (VIII). A solution of 6 g of N-bromomorpholine in 85 ml of benzene was added dropwise over 1·5 hours to a solution of 5·45 g of I in 20 ml of morpholine at 30–40°. The colourless precipitate that separated was filtered off, washed with water and dried. This yielded 6·5 g of VIII (76% of theory) of m.p. 206–209°. The melting point was unchanged after recrystallization from alcohol.

Found, %: C 56·49; 56·65; H 5·77; 5·75; S 13·43; 13·57.
$C_{11}H_{13}N_3OS$ Calculated, %: C 56·40; H 5·60; S 13·60.

2-(p-Tolylaminomethyl)benzimidazole (IX). A solution of 30·5 g of *p*-toluidine and 23·6 g of 2-chloromethylbenzimidazole in 100 ml of absolute alcohol was heated under reflux for 3 hours and then evaporated until a deposit formed. This was filtered off after cooling. After addition of 50 ml of 10% NaOH the deposit was steam distilled to remove unreacted *p*-toluidine and the new residue (the almost pure reaction product) was recrystallized from a mixture of alcohol and acetone. This gave 30 g of IX (yield 90% of theory) of m.p. 175–176°.

Found, %: C 75·41; 75·28; H 6·38; 6·28.
$C_{15}H_{15}N_3$. Calculated, %: C 75·96; H 6·33.

2-(β-Naphthylaminomethyl)benzimidazole (X). A solution of 28·6 g of β-naphthylamine and 16·6 g of 2-chloromethylbenzimidazole in 100 ml of absolute alcohol was refluxed for 2 hours. After removal of β-naphthylamine by boiling with water the residue (the free base X) after several recrystallizations from a mixture of alcohol and acetone had m.p. 210°–220° (with decomposition). The picrate of X after recrystallization from alcohol had m.p. 230°–231° (with decomposition).

Found, %: C 57·40; 57·43; H 3·41; 3·56.
$C_{24}H_{18}N_6O_7$. Calculated, %: C 57·40; H 3·58.

CONCLUSIONS

(1) Some derivatives of benzimidazole have been synthesized and their efficiencies as inhibitors of the oxidation of polypropylene have been studied.

(2) It is shown that in derivatives of benzimidazole containing the functional groups —SH and >NH, the sulphydryl group is responsible for the inhibiting efficiency.

(3) It is shown that in mixtures with *p*-hydroxyphenylamine the synergistic

effect falls in the order of compounds containing —S—S—, —SH and —SN< groups. Here the maximum synergistic effect is shifted in the direction of large concentrations of the benzimidazole derivatives.

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THE OPTICAL POLARIZATION METHOD FOR DETERMINATION OF STRESSES IN POLYMERIC MATERIALS—III. THE EFFECT OF VARIOUS FACTORS ON THE OPTICOMECHANICAL PROPERTIES OF THE POLYMERIZATION PRODUCTS OF A TERNARY VINYL MONOMER SYSTEM*

T. V. SHAMRAYEVSKAYA and S. I. SOKOLOV

Moscow Institute of Chemical Plant Construction

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IN ONE of our previous communications [1] we studied the dependence of a number of physical properties, including optical sensitivity (strain birefringence) on the state aggregation and structure of polymers. For this purpose we chose the more

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